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RESEARCH AND DEVELOPMENT STUDY OF THE SILVER-CADMIUM  
COUPLE FOR SPACE APPLICATION

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## P U R P O S E

The goal of this contract is to provide an insight into basic problems associated with the operation of the sealed silver oxide-cadmium system, under satellite operating conditions. At the end of the contractual period the information will be used to design, construct, and deliver an improved 30-cell battery to NASA.

ABSTRACT

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Two groups of cells operating on the short and long orbit regimes have completed 900 and 75 cycles respectively. A recent deep discharge showed that lowering the positive plate density has a beneficial effect on cell capacity.

Difficulties have resulted from cycling cells of different construction as multi-cell batteries. Differences in capacity have led to overcharge in individual cells and excessive pressure rise. This difficulty has been overcome by construction of a cycler with automatic cutoff for each cell.

Several cells which feature a combination of Cl<sub>9</sub> and PVA with a separator inert to oxidation by silver have completed 50 high rate deep cycles at 50°C with excellent capacity maintenance; the controls shorted at cycle 35.

A 50°C stand test to correlate attack by silver with change in composition of the electrolyte has been discontinued after 100 days. The results indicate that the cells built with a combination of PVA and Cl<sub>9</sub> as against PVA or Cl<sub>9</sub> alone, produce the largest quantities of soluble organics. The possibility of decreasing the amount of organics in the KOH is being studied in cells fabricated with separators especially prepared with this objective in view.

The performance of cells fabricated with partially wet-proofed cadmium electrodes appears to be satisfactory after 400 shallow short orbit cycles. The oxygen recombination rate has decreased somewhat but is still much larger than in the controls.

In an effort to eliminate hydrogen evolution in sealed cells during charge and overcharge, different methods of formation charging are being evaluated. Preliminary results show that a change of less than 80% of theoretical negative capacity is desirable on cycle one.

Results from chemical and electro-chemical tests on cycled negative electrodes have definitely shown that partial inactivation occurs during cycling because of carbonate accumulation in the electrolyte and in the plate itself. There is also evidence that the cadmium metal "ages" through a re-crystallization process.

Cells containing various means for improving argentous operation have completed 65 cycles, maintaining about 60% of theoretical argentous capacity on the long orbit. Cells on the short orbit were discontinued after 20 cycles because of poor performance.

*H. Altman*

## BODY OF THE REPORT

### 1. Phase 1

#### 1.1 Cell Tests

Thirty-six cells which include variations in electrode density, separator system, and electrolyte concentration are presently being cycled on the 100 minute and 24 hour orbital regimes. They have completed 900 and 75 cycles respectively. A few cells from the short orbit group were removed after 600 cycles because of the development of excessive pressure. The difficulty arose from the fact that cells of different constructions were cycled as batteries, with the battery voltage only being monitored. Differences in capacity would result in gassing in those cells reaching full charge first.

This difficulty has been overcome through the use of an automatic scanning device which removes cells from the charge circuit when their preset voltage is reached. One of the exploded cells was dissected to determine why prolonged cycling of silver-cadmium cells reduces the negative electrode efficiency, and eventually produces a condition where hydrogen evolution occurs during charge or overcharge. The negatives were removed, washed in cold water for three hours, dried under nitrogen and then weighed. One electrode was chemically analyzed and two were assembled as individual negative-limiting cells which were filled with fresh 42% KOH.

To determine the composition of the negative electrode, the plate which weighed 5.1 g was partially dissolved in a 25% solution of ammonium hydroxide ( $\text{NH}_4\text{OH}$  reacts with  $\text{CdCO}_3$  and  $\text{Cd}(\text{OH})_2$  but does not attack Cd metal which had previously been standardized with 0.1 N HCl to determine the stoichiometric end points for  $\text{OH}^-$  and  $\text{CO}_3^{2-}$ . The electrode was removed from the solution after two hours and then washed, dried, and re-weighed. The ammoniacal solution was again titrated with 0.1 N HCl to the phenolphthalein and methyl orange end points. The increase in carbonate in the ammonium hydroxide corresponded fairly closely with the loss in weight of the cadmium electrode; the difference was taken to be  $\text{Cd}(\text{OH})_2$ . The composition was 81% Cd metal, 17%  $\text{CdCO}_3$ , and 2%  $\text{Cd}(\text{OH})_2$ .

The two electrodes fabricated into partial cells were tested as follows:

One cell was given three cycles at 100 ma/in<sup>2</sup> discharge and 65 ma/in<sup>2</sup> charge. A eudiometer and a Hg/HgO reference electrode were attached to the cell to determine the gassing potential. Two control cells with fresh cadmium electrodes were also cycled in a similar manner. Figure 1 shows the discharge curves for both electrodes, and Figure 2 shows the charge curves during the three cycles. The potential of the negatives during charge showed that the cycled electrode began to evolve hydrogen when the input was 60% of the total charge accepted, while the control cell charged efficiently to about 85% of the input before hydrogen was evolved. Charging was terminated at -1.35 volts vs the mercuric oxide electrode.

It should be noted that the capacity of the cycled negatives increased at this charging rate, which corresponded to the shallow cycling charge rate; evidently the fresh electrolyte was responsible. Even with the increase in capacity for the cycled negatives, only 48% of the metal content of the plate functioned electrochemically.

In a similar set of experiments, a cycled electrode and a control negative were charged at 19 ma/in<sup>2</sup> and discharged at 100 ma/in<sup>2</sup> for three cycles; the results are presented in Figures 3 and 4.

A chemical analysis was performed on one control negative which weighed 4.45 g after the first charge; the results showed 91% Cd metal, 7% Cd(OH)<sub>2</sub> and 2% CdCO<sub>3</sub>. It can be seen from Figure 3 that the electrical data are in fair agreement with the chemical analysis for the first charge.

By using a low rate charge, the working fraction of the cycled electrode was increased to 65%. Chemical analysis of the old negative after the third charge showed 90% Cd metal, 7% CdCO<sub>3</sub>, and 3% Cd(OH)<sub>2</sub>. Note that 10% of the CdCO<sub>3</sub> was charged at 19 ma/in<sup>2</sup>. Although low rate charging appears very beneficial in improving capacity there is still about 20% of the Cd metal which remains inactive. During cycling cadmium is believed to undergo recrystallization to larger particles, which lowers the surface area of the electrode. This phenomenon is being studied in electrodes which have received 1000 cycles, by means of AC transients, and by metallographic microscopy.

Included in this study are cycled impregnated Cd in nickel plaque electrodes which are reported to retain their activity for a longer period than do sponge electrodes.

A reactivation procedure which has proved successful with pasted negatives is a low rate charge (or overcharge) followed by a low rate discharge and drain. This method will be investigated with these heavily cycled negative plates which are of pressed construction.

As one of the construction parameters being studied, cells were built with variations in positive electrode density. Each pair (5&6, 7&8, 9&10) contained positive plates made with "HC" silver and pressed to one of the three densities, 3.6, 4.2, and 4.8 g Ag/cc. The negatives were cadmium oxide, mold pressed to 2.8 g Cd/cc. The separator system was (+)2NI/6Cl9 and all cells were filled with 42% KOH. The even numbered cells are being cycled on the 100 minute regime and the odd numbered cells on the 24 hour regime.

The cells were initially given several deep cycles at room temperature,  $-15^{\circ}\text{C}$ , and  $+50^{\circ}\text{C}$  at the above rates, during which time differences in capacity were small (see Report #3 Phase I - Cell Tests). However, a deep discharge after 750 and 70 cycles, on the short and long orbit regimes respectively, showed that cells with the lowest density silver (3.6 g/cc) were delivering about 30% better capacities than cells fabricated with plates pressed to 4.8 g/cc - see Figure 5. It should be noted that the lower density silver is more effective on a volume basis as well as a weight basis.

Deep discharge results on the remaining cells after 750 and 70 cycles on the short and long orbit regime are shown in Tables I and II.

As can be seen, the cells on short orbit regime show better capacity maintenance than those on long orbit regime. It appears that charging time rather than the number of cycles determines the life of a cell. The mechanism may be through silver attack on membranes or change in electrolyte concentration. This will be investigated.

The long orbit cells have completed 70 cycles which represents a total charge time of  $70 \times 23$  or 1610 hours, while cells on the 100 minute regime charge for 1.08 hours on each cycle which equals  $750 \times 1.08$  or 810 hours of charging time.

Data obtained from 8-cell batteries run at  $5^{\circ}$ ,  $25^{\circ}$ ,  $35^{\circ}$ , and  $50^{\circ}\text{C}$  by Inland Testing Corp. under Air Force Contract #33(616)-7529 - contractor Yardney Electric Corp. afford additional information concerning cycle life as a function of depth of discharge. The results presented in Figures 6 and 7 indicate that time-to-failure as well as cycles-to-failure decreases as depth of discharge is increased. Also, time life is roughly twice as great for cells on the 24 hour orbit. It is significant that the best performance on the 24 hour orbit regime was given by the cells operating at  $5^{\circ}\text{C}$ , the lowest temperature studied. On the two-hour orbit, however, the cells failed because of difficulty in charging at the required rate. The difficulty increased rapidly with increasing depth of discharge.

## 1.2 Changes in Properties of Separator

### Materials

Six cells were built during the last quarter to investigate the properties of various cellulosic and non-cellulosic separator materials. The cells were fabricated with standard positive and negative electrodes, and filled with 42% KOH. They vary in type of separator system used as follows:

Cell #	Separator System
150	(+)1NY/2Visking (Fibrous)/(-)/1 Viskon R-75D
151	(+)1NY/6PUD-0-300/(-)/1Viskon R-75D
152	" " " /(-)/1Pellon-10 mil
153	(+)1M406/3Visking/(-)
154	(+)1M401/1Poly-Por-Wa/1Visking Fibrous/(-)/1Pellon-10 mil
155	(+)1M470/2XPE40/50/4Permion 600/(-)/1M410

The M400 series and M470 materials are nylon and dynel cloths supplied by Kendall Corp. The XPE 40/50 is a radiation grafted polyethylene and Permion 600 is a grafted cellophane supplied by Radiation Applications, Inc.

The cells were given a low rate formation charge, sealed, fitted with pressure gauges and then given several deep cycles at room temperature and -15 C at rates equivalent to the 100 minute orbital regime. The deep discharge data are plotted in Figures 8 and 9. It can be seen that cell 153 is performing the best at both temperatures tested. The lower resistance separator system is probably the principal factor here. The cell made with materials from RAI appears to be the poorest; this correlates with the fact that the wet resistance of the films were quite high. After a deep discharge cycle at +50 C the cells will be life cycled on the 100 minute regime.

A 100-day stand test at 50°C was run to determine whether separator attack by silver could be correlated with the organic salt content in the electrolyte. Results obtained during this contractual period have shown that performance and gas recombination are hindered in sealed cells when organic cadmium salts (measured as  $\text{CdCO}_3$ ) are formed by the reaction of  $\text{Cd(OH)}_2$  with soluble organic debris.

For the 50°C stand test cells were fabricated with various separator systems, including PVA, Cl9, and films produced by Radiation Applications Inc. Results of the electrolyte analyses are shown in Figure 10. The cells were initially filled with much more than the standard quantities of electrolyte to provide enough sample material for analysis over the period of the test. Since the ratio of electrolyte to pack volume was much greater than in normal cells, some silver oxide could diffuse through the KOH over the top of the separators instead of being restricted to reaction through the outer layer of separator only. The reaction rate was therefore greater than would be expected in a normal cell at this temperature.



The data shows that the degradation rate is about twice as great for systems containing PVA as for those with Cl9 only. The XPE films also show a low degradation rate. Samples of electrolyte have been taken from each cell for infra-red analysis to determine the type of organics which are present; results will be given in the next quarterly report.

In an effort to minimize the soluble organics from the separator, Yardney Chemical Co. submitted Cl9 and Visking sausage casing to a treatment which caused a weight decrease of about 5%. The treated Cl9 is termed S-1-51-1. Cells were built using both materials.

The cells were placed in the charged state in an oven at 50°C to measure the extent of separator attack. Results after two weeks indicate that cells with treated separators show little if any increase in electrolyte carbonate. The test is continuing; the cells will eventually be cycled. Several cells are also being built with XPE in combination with the treated separators to be tested as above.

In another separator test, cells were fabricated using a special wrap with one RAI-XPE 40-50 positioned between turns of the main separators, which were either Cl9 or PVA. The objective here is to use the inert film to interrupt the continuous silver trails which normally form through PVA and regenerated cellulose and thus to extend cell life.

The cells are being deep-cycled at rates equivalent to the 100 minute orbit at 50°C, and are left standing charged at frequent intervals to observe whether shorting has occurred. The data in Figure 11 show that the two cells with XPE are delivering good capacity after 50 cycles; the two controls developed shorts after 37 cycles and were discontinued. These data therefore look promising with respect to the use of XPE for this purpose.

### 1.3 Effect of Electrolyte Quantity on Cell Performance

#### Cell Performance

Results from Report No. 3 have shown that the oxygen recombination rate roughly doubles when all the "free" electrolyte is removed from a cell but a loss of at least 30% of the initial capacity is also incurred. However, in recent experiments the capacity of cells has been significantly improved by substituting highly absorbent Pellon for the nylon around the positive and negative. Three cells were built with (+) 1 Pellon (4 mil)/4Cl9/(-)/ 1 Pellon (10 mil) and filled with 18 ml of 42% KOH. After a formation charge, 5% of the total quantity of electrolyte was removed from one cell, all the free electrolyte (10% of the total) was removed from a second cell, and none was removed from the third. The cells were then sealed and fitted with pressure gauges.

The performance after four high rate deep cycles at room temperature,  $-15^{\circ}\text{C}$ , and  $+50^{\circ}\text{C}$  is shown in Table III. It is evident that the quantity of Pellon used held enough electrolyte so that removal of the free electrolyte did not adversely affect cell capacity over the small number (6) of cycles run thus far.

The oxygen recombination rates were determined after cycle 4. The cells were evacuated and then filled with oxygen. The rate of oxygen recombination was calculated by plotting  $\log \frac{dP}{dt}$  versus  $\log P$ ; data are presented in Fig. 12.

The results indicate that a cell with saturated Pellon gives an oxygen recombination rate substantially equal to that of a Pellon-free cell when neither has any free electrolyte. The rate at 45 psia and room temperature is equivalent to a current density of about 3 ma/in<sup>2</sup>. The cells have been placed on the 100 minute orbit regime for life performance data. Several multi-cell batteries incorporating Pellon will also be built. The objective here is to determine how inter-cell balance is maintained during cycling when free electrolyte is removed. Hydrogen and oxygen recombination will also be investigated in these units.

## 2. Phase 2 - Gas Recombination

### 2.1 Gas Recombination in Cells

As was described in the 3rd quarterly report, oxygen recombination on wet-proofed cadmium plates proved to be about 100% more rapid than on untreated plates. Following the experiments with individual plates, four cells were built with treated cadmium negatives. Three of these had Pellon interseparator systems with three different amounts of electrolyte. The fourth was built with nylon and Cl9, and contained a normal quantity of electrolyte.

After a series of capacity evaluation cycles, (see Table IV), the cells were overcharged at various current densities to determine the recombination rate at equilibrium pressure, and also to establish the maximum allowable current for continuous charging. The results are given in Figure 13. After 400 shallow cycles the oxygen recombination rates were again determined on the two cells with nylon interseparator; the results show that the rates had decreased by over 50%. Experiments discussed in the previous report showed that organic products and  $\text{K}_2\text{CO}_3$  resulting from separator attack reduced the oxygen recombination rate by a factor of 2.5. However, the recombination rates obtained after prolonged cycling will still enable safe sealed operation for the low charge rates encountered during constant potential charging.

The results of this cycle test are also important from a capacity standpoint, since they show that the wet-proofing additive does not have a detrimental effect on cell performance, (see Table IV).

## 2.2 Effect of Extent of Negative Formation on Gas Evolution

Data obtained from the NASA laboratories indicate that hydrogen as well as oxygen is evolved at the end of normal constant current and constant potential charging of a YS-5 sealed battery. Since the hydrogen reaction rate with silver is much lower than oxygen recombination with cadmium, safe sealed operation becomes a severe problem. The problem is under attack by way of a study of the effect of the extent to which the negative is charged on the first, so-called formation, cycle.

Three YS-5-I cells containing 3 positives and 4 negatives were initially charged at 20 ma/in<sup>2</sup> to 60, 80, and 100% of the theoretical negative capacity (which is 8.85AH) respectively; two additional cells were charged to 1.60 volts and 1.9 volts respectively. Charge curves are shown in Figure 14. The five cells were then discharged at the eight hour rate (500 ma) to 0.6 volts. The discharge curves are shown in Figure 15. The curves indicate that there is some progressive small gain in capacity on the first discharge as a result of increasing the conversion of the cadmium oxide from 60% up to 90% (corresponding to charge to 1.90 volts). The cells were then given 3 cycles consisting of charge at 0.91 A to 1.65 V and discharge at 1.7 A to 0.6 V. These are the rates of the 100 min orbit. Figure 16 shows the results. It is evident that the cell charged initially to 80% of the cadmium capacity is doing virtually as well as those charged to a greater extent. However, for prolonged shallow cycling, the cells charged to a lesser extent may prove more satisfactory since the greater quantity of cadmium oxide remaining may provide a better margin of safety against hydrogen evolution. The cells have been placed on the 100 min orbit automatic cycler to determine the long-term effect.

## 2.3 Trickle Charging

NASA had reported that the initial pressure rise which occurs in a sealed cell on trickle charge is followed by a sharp decrease rather than the expected leveling-off. To study this phenomenon, cells 44 and 50 with a normal quantity of electrolyte and cells 41 and 50, from which all free electrolyte had been removed, were placed on trickle charge at a rate of 0.1 ma/in<sup>2</sup>.

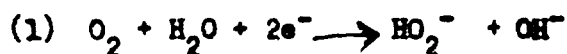
After 80 days on charge, the pressure in cells 41 and 50 began to fall. The pressure in cells 44 and 46 which contained a normal quantity of electrolyte became excessive after 80 days of operation, making it necessary that they be discontinued.

A few analyses of the gas were made; these indicate a relationship between pressure decay and decrease in hydrogen concentration. See Fig. 17. The analytical technique has been inadequate in that samples were necessarily very small. A new sampling device is under construction which is designed to take samples without contamination by air. Pressure changes will then be related to gas composition, individual electrode potentials, temperature and possibly to electrolyte composition. Most of these tests will be run in multi-cell batteries.

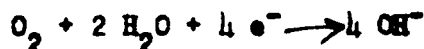
It should be noted that it was reported in the third quarterly that hydrogen scavenging is slow in cells with normal electrolyte quantity (cells 44 and 46). There does not seem to be much point to studying intermediate quantities of electrolyte in cells with Pellon.

#### 2.4 Reduction of Oxygen on Negative Electrodes

At negative potentials, the reduction of oxygen on mercury is known to proceed through two electrochemical steps:



The overall reaction is



As is to be expected, the two waves of a volt-ampometric curve for reduction of oxygen on mercury are of equal height.

The reduction of oxygen on solid metals may be more complex because of the possibility of catalytic effects. We started our work with silver which is known to catalyze the decomposition of peroxy ion. A smooth silver disc with a two-side area of 4 cm<sup>2</sup> was rotated at 1440 RPM. The electrolyte was saturated with oxygen at atmospheric pressure prior to each run. Figure 18 shows the curves obtained with 31% & with 38% KOH.

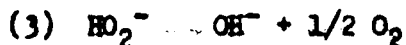
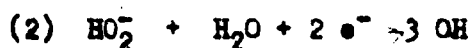
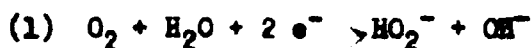
The results show that the overall reaction rate as indicated by the height of the second wave is 2.7 times as great in 31% KOH as in 38% KOH, being 0.150 ma/cm<sup>2</sup> for 31% KOH and 0.055 ma/cm<sup>2</sup> for 38% KOH. The fact that the plateaus are horizontal and thus insensitive to electrode potential is consistent either with a diffusion limited reaction or with a multiple step mechanism in which the limiting reaction is chemical. However, no such multiple step mechanism is immediately apparent; moreover, the measured reaction rate corresponds well with the rate calculated from the diffusion current equation and the Levitch equation. For 31% KOH, the calculated rate is 0.32 ma/cm<sup>2</sup> and the measured rate was 0.150 ma/cm<sup>2</sup>. This would indicate that the reaction is diffusion limited.

The expression used is  $I_d = \frac{nFDC}{\delta}$

D is the diffusion constant

and  $I_d$  is the diffusion current,  $n$  is 4 for oxygen,  $F$  is the faraday,  $C$  is the bulk concentration of oxygen, and  $\delta$  is the thickness of the diffusion layer. The smaller reaction rate in 38% KOH is then due in part to the greater viscosity of this solution, and also to the lower oxygen solubility. It should be noted that a diffusion limited current is independent of the material used.

It is significant that the second wave of each curve on silver is smaller than the first. This indicates that a catalytic step is involved in the reaction. The following mechanism is suggested.



Step (3) is the catalytic decomposition of  $\text{HO}_2^-$  which takes place simultaneously with the electrochemical reduction. In the process, oxygen is regenerated; this oxygen must be reduced again, thus accounting for the greater height of the first wave.

It is important to realize that the increase in height of the first wave is compensated for by the decrease in height of the second. This must be the case, since the number of electrons transferred in the overall reaction remains constant. The limiting step is the diffusion of oxygen from the bulk of the solution to the electrode. The fact that some of the peroxy breaks down catalytically at the electrode surface can only result in a change in the fraction of the total number of electrons transferred in each step but not in the total number itself or in the oxygen diffusion rate. Finally, the overall reaction rate on amalgamated silver, which shows two nearly equal waves, is the same as on untreated, catalytically-active silver.

Only one run has been made on nickel (Fig. 19). The curve is quite different from those of silver or of mercury, showing only one plateau. With increase in potential, hydrogen evolution begins, completely eliminating the second wave. Evidently, the peroxy ions produced in the first stage are reduced by the hydrogen evolved as the electrode potential is increased. This point is particularly important with respect to operation of the cadmium electrode since this electrode normally charges at a potential near -0.9 volts. In a silver-cadmium cell, where the cadmium may approach full charge simultaneously with the silver electrode, it may therefore be important to avoid nickel as the additive for conductivity, in order to avoid production of hydrogen. Of course, where the positive reaches full charge first, the nickel may catalyze recombination of oxygen by production of adsorbed hydrogen atoms.

In voltamperometric measurements on silver and on nickel, the curves showed one or more plateaus, so that the limiting current could be determined directly. With cadmium, the situation is different since there is no plateau which can be attributed to a single process. Rather, in the potential range of interest, hydrogen is evolved simultaneously with reduction of oxygen.

To overcome this difficulty, the actual rate of removal of oxygen by a rotating cadmium disc was measured, and the corresponding current density was calculated. For the measurements, the rotation was stopped and a dropping mercury electrode curve was run to determine the residual oxygen in the solution. Oxygen recombination with the halted disc during this period was found to be negligible, which is reasonable in view of the much greater thickness of the diffusion layer on the stationary disc.

Table V shows the data for cadmium as well as for silver. The rate of recombination on cadmium is sensitive to the electrode potential, and is also much lower than for silver which we have shown to be diffusion limited. It follows therefore that the reaction with cadmium is kinetically limited.

At open circuit, the electrons for the reduction of oxygen must be derived from the cadmium; this reaction is essentially chemical. As the electrode potential is made more negative, the extent of the chemical reaction decreases, to be supplanted by the electrochemical reaction. Table V shows that the rates at open circuit and at  $-0.85$  are identical. The potential difference for the two states is only a few millivolts.

This extremely interesting work is still in an early phase. If time permits we hope to measure the effect of catalysts, temperature, and adsorbed impurities.

### 3. Phase 3 - Constant Potential Charging

The loss of argentic voltage as a result of prolonged constant potential charging is being investigated in this phase of the program.

To determine how the percentages of  $\text{AgO}$ ,  $\text{Ag}_2\text{O}$ , and  $\text{Ag}$  influence the reactions governing loss of the upper plateau voltage during constant potential charging, several cells were given a ten week "float". Following the charge the cells were dissected and the positive plates chemically analyzed. The results of the polarographic analyses, however, indicated unusually high concentrations of  $\text{Ag}_2\text{O}$  in all the samples that were tested. These findings were contradictory to those of Dirkse and Wales who found, by X-ray diffraction, very little if any  $\text{Ag}_2\text{O}$  remaining in the plates after extended periods of constant potential anodization. The polarographic technique used in our work has since been improved to deal with the small concentrations of argentous oxide encountered during long c.p. charging.

At present, 12 cells which include different positive electrode constructions and lead additives are on "float", and will shortly be analyzed for changes in positive plate composition.

#### 4. Phase 4, Argentous Level Operation

The effects of conductive additives to increase the argentous efficiency are being studied in this phase of the program.

Cells were constructed with HC, FR, and MR silver powders mold pressed to 4.8 g Ag/cc. The silver powders were initially "doped" with either palladium or lead before being fabricated into electrodes. The cells are presently being cycled on the 24 hour orbit regime.

After 65 cycles, the cells made with MR and FR silvers plus 1% Pd appear to be performing the best, delivering about 55-60% of theoretical  $\text{Ag}_2\text{O}$  utilization. The data for all the cells are presented in Figure 20. Caution must be taken of the fact that cells constructed with FR & MR powders but without lead or palladium lose their long argentous properties after 10-15 cycles. It should also be noted here that conductive additives which were tested (graphite, Shawinigan Black, and carbonyl nickel) did not extend the lower level operation of the cells.

Cells are presently being designed which will incorporate the best features of both lead and palladium treated powders. Consideration is also being given to the use of low density electrodes, which were found to be superior on orbital testing.

A new type of positive electrode which features a highly porous nickel matrix is being evaluated in a sealed cell; the electrode contains a lead additive to decrease the oxygen evolution rate during charge. The cell is being evaluated on a deep cycle regime at rates equivalent to the 100 minute orbit. After 48 cycles the cell is delivering 68% theoretical utilization of active material with 38% of this available on the argentic plateau.

Experiments have shown that the optimum weight of silver in the nickel matrix corresponds to 27-30% of the void volume of the matrix. The capacity density achieved is about 17.5 AH/in<sup>3</sup> of electrode as compared with 23 AH/in<sup>3</sup> for a standard silver plate.

## PROGRAM FOR FIFTH QUARTER

### Phase I General Cell Study

Study the physical and chemical changes taking place in the sponge cadmium negative, as a result of extended cycling with particular reference to change in particle size and area and change in chemical composition. Correlate with decrease in material utilization. Investigate low rate charge and discharge as a method of restoring capacity loss. Construct and cycle cells with impregnated negatives, and compare performance with sponge negatives.

Continue the investigation of the separator S-1-51-1 as a means of decreasing the formation of passive cadmium and cadmium salts. Determine the effect of separator debris on cycling performance and on performance after discharged stand. Determine the effect of the interposition of inert separator and interseparator material on the rate of oxidation of separators by silver oxide.

### Phase II Gas Recombination

Study the effects of interseparator, electrolyte quantity and wet-proofing on hydrogen and oxygen recombination in multi-cell batteries in which differences in the state of charge between cells will be an additional factor. Continue the study of the effect of temperature and of electrolyte concentration and quantity in individual cells and also in batteries.

Continue the study of the conditions leading to evolution of hydrogen with particular reference to initial formation of electrodes, decrease in material utilization and the effect of adsorbed and reacted organic material. Determine cathodic Tafel curves on  $\text{CdO}$ ,  $\text{Cd}(\text{OH})_2$  and  $\text{CdCO}_3$ , both fresh and cycled. Determine anodic curve on fresh and on cycled  $\text{Cd}$ .

### Phase III Constant Potential Charging

Use improved voltamperometric method for analyses of charged silver plates with respect to content of  $\text{Ag}$ ,  $\text{Ag}_2\text{O}$  and  $\text{AgO}$ . Determine the electrical resistance of the silver plate at various stages of oxidation.

### Phase IV

Continue cycling single cells on long orbit regime. Study the possibility of using  $\text{Pd}$  and  $\text{Pb}$  in combination for extended argentous and argentic capacity. Determine the effect of low electrolyte concentration and low positive plate densities on "doped" MR and FR silver powders. Continue cycling silver impregnated nickel cells on an accelerated regime. Build cells with  $\text{Pd}$  and  $\text{Pb}$  in combination with nickel matrix.



DISCHG. PERFORMANCE OF CYCLED NEGATIVES  
 (AFTER 600 SHALLOW CYCLES)  
 $I_D = 100 \text{ ma/in}^2$

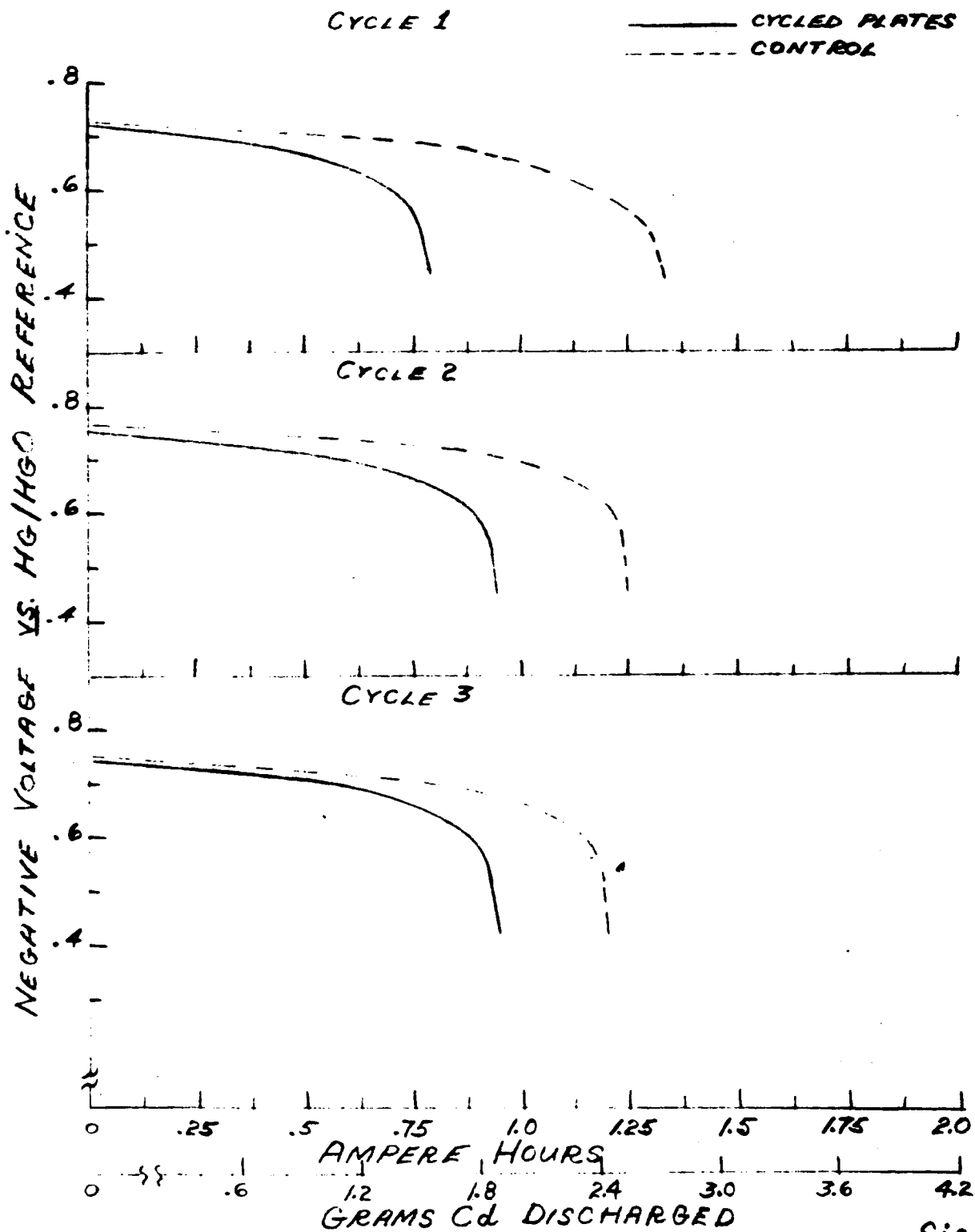


Fig. 1

# CHARGE PERFORMANCE OF CYCLED NEGATIVES (AFTER 600 SHALLOW CYCLES)

$I_c = 65 \text{ ma/in}^2$

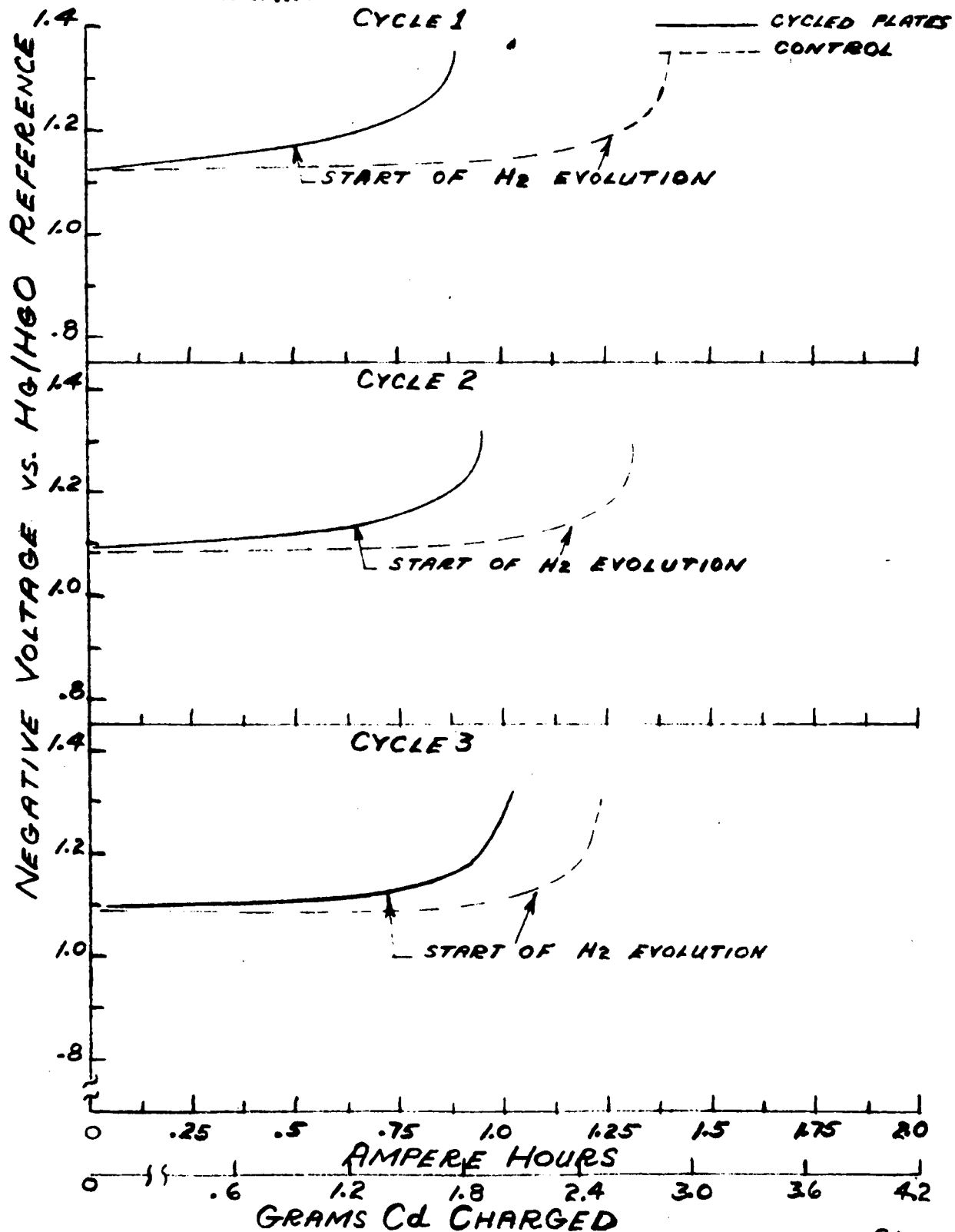
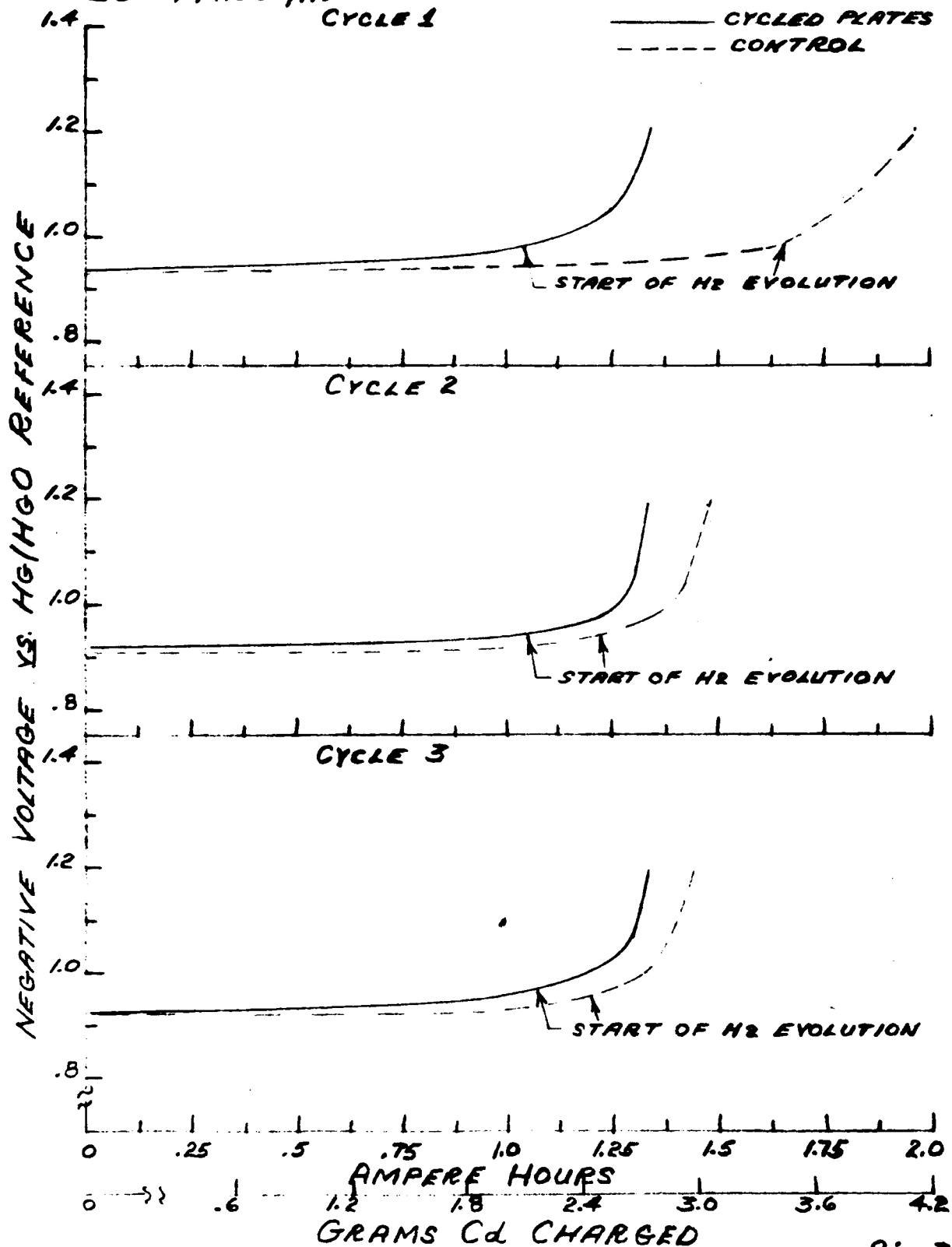


Fig. 2

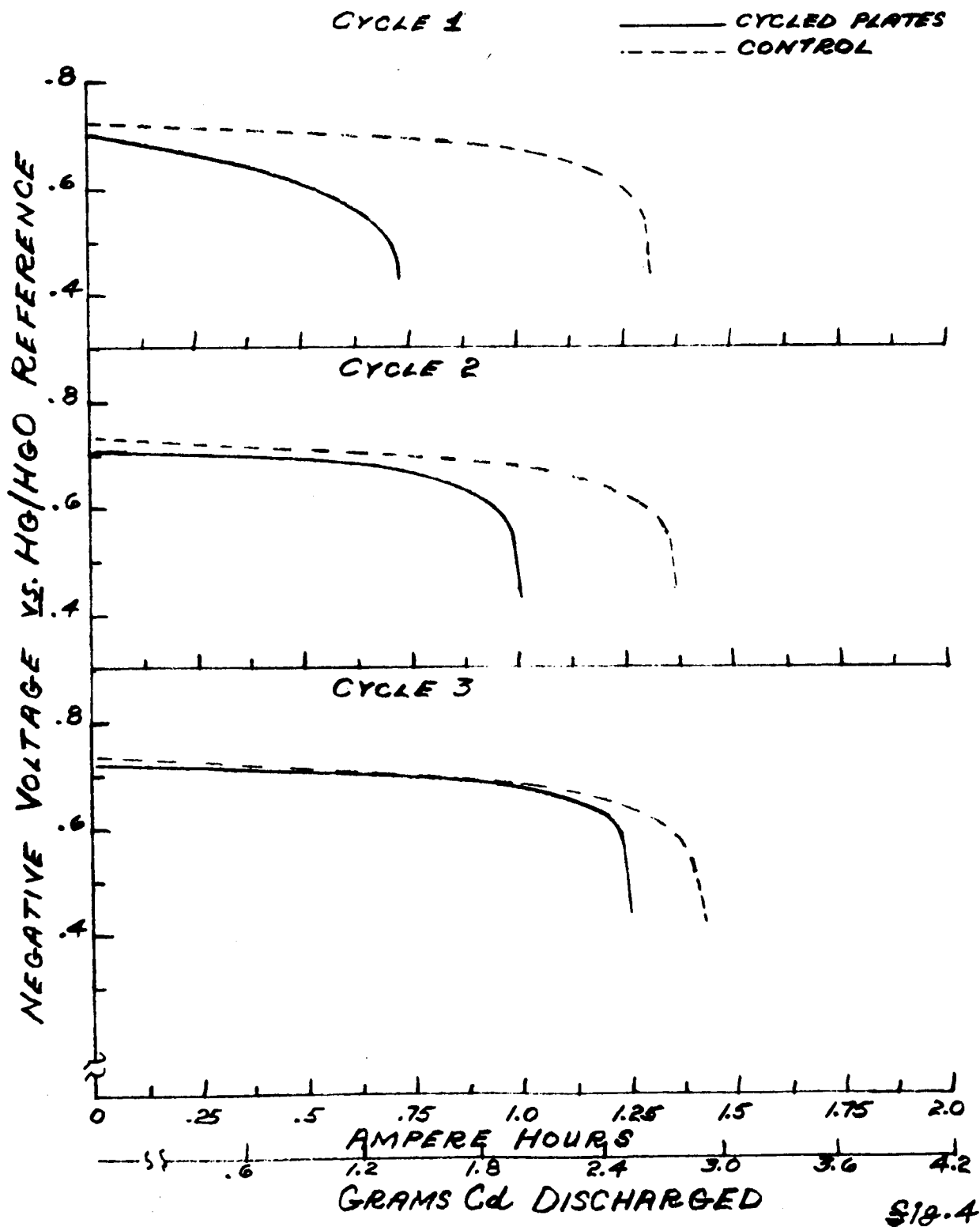
# CHARGE PERFORMANCE OF CYCLED NEGATIVES (AFTER 600 SHALLOW CYCLES)

$I_C = 19 \text{ mA/in}^2$

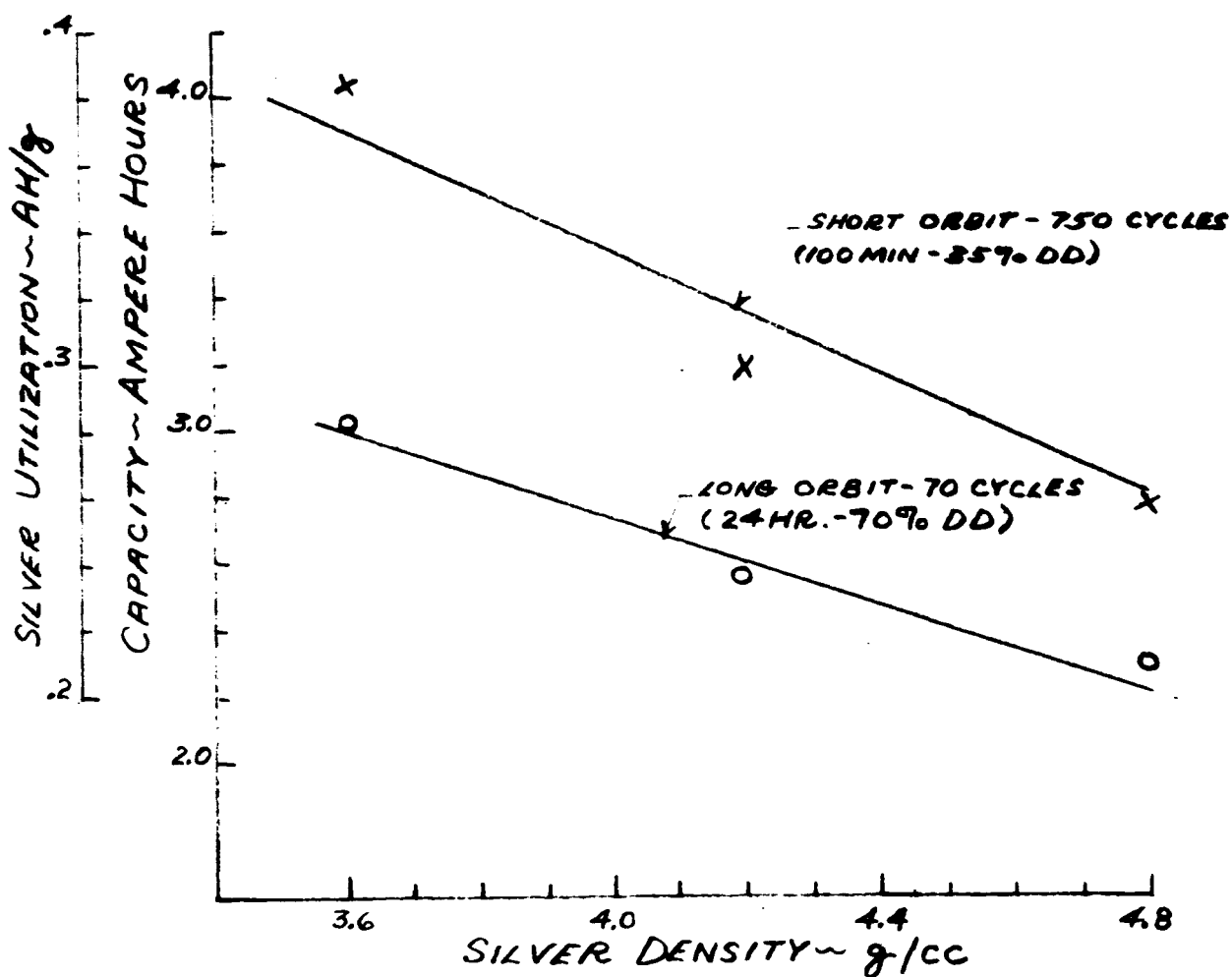


DISCHG. PERFORMANCE OF CYCLED NEGATIVES  
(AFTER 600 SHALLOW CYCLES)

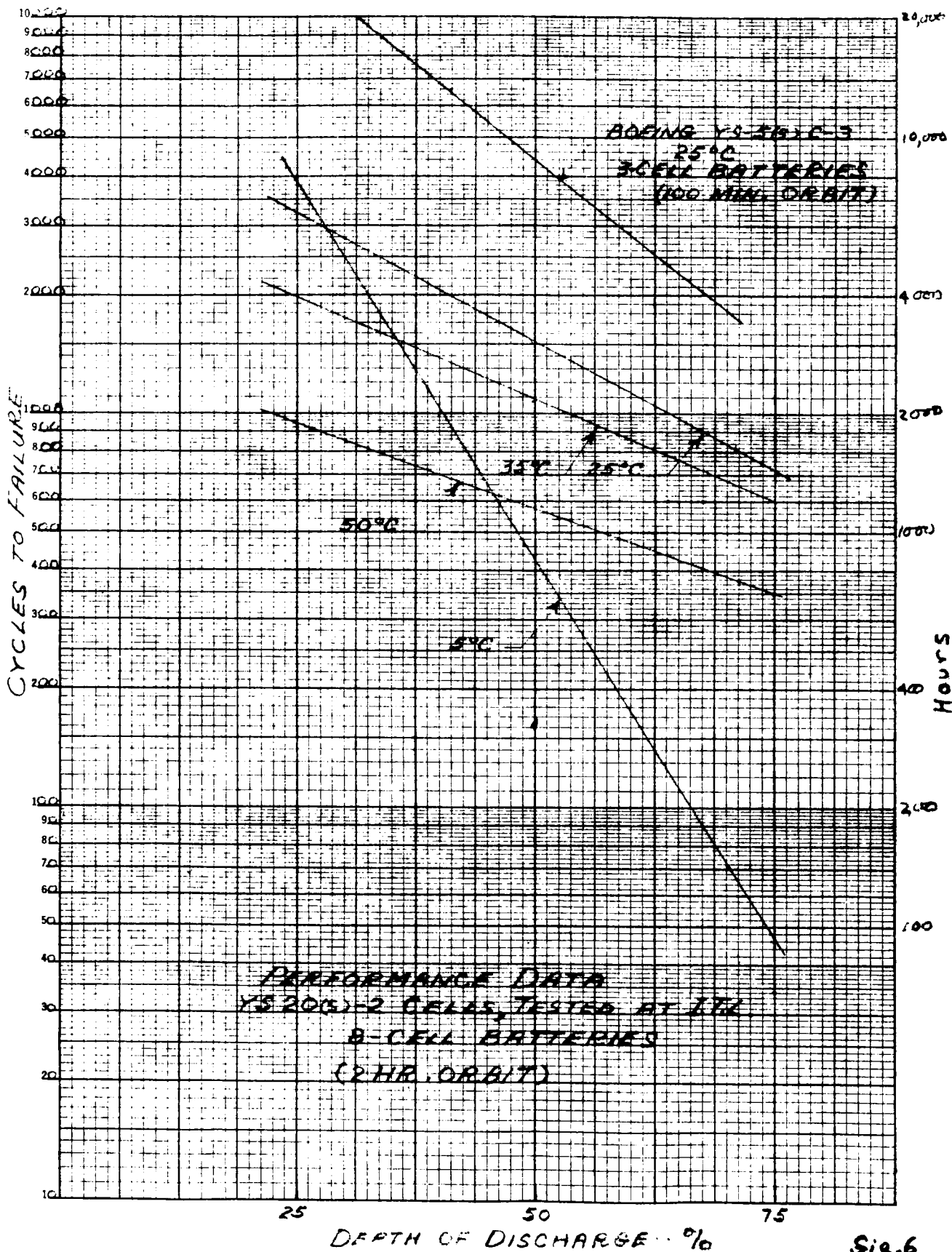
$I_D = 100 \text{ mA/in}^2$



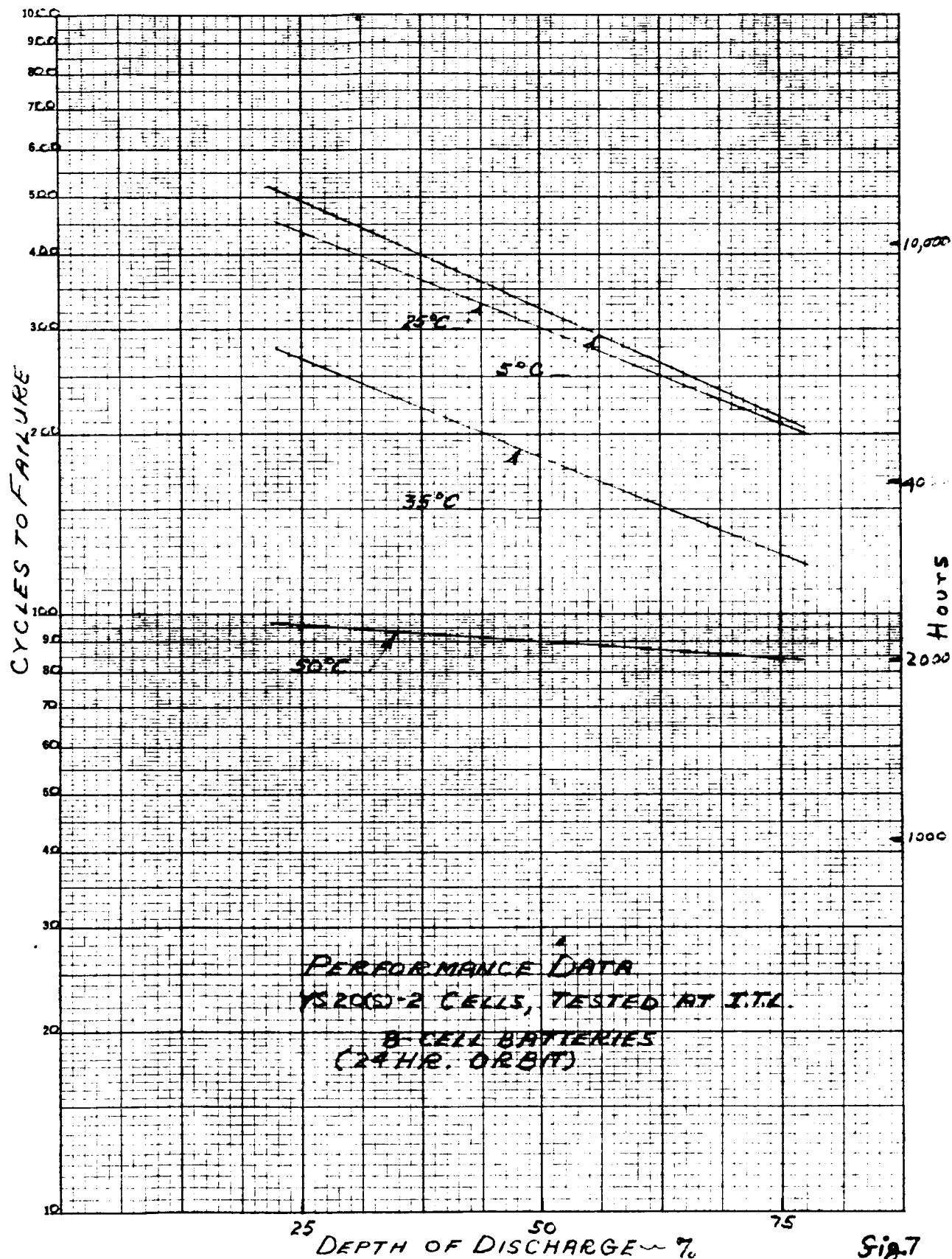
# EFFECT OF SILVER DENSITY ON PERFORMANCE (SEALED Ag-CL CELLS)



NOTE x CELLS WERE (+) LIMITED ON DISCHARGE  
o CELLS WERE (-) LIMITED ON DISCHARGE



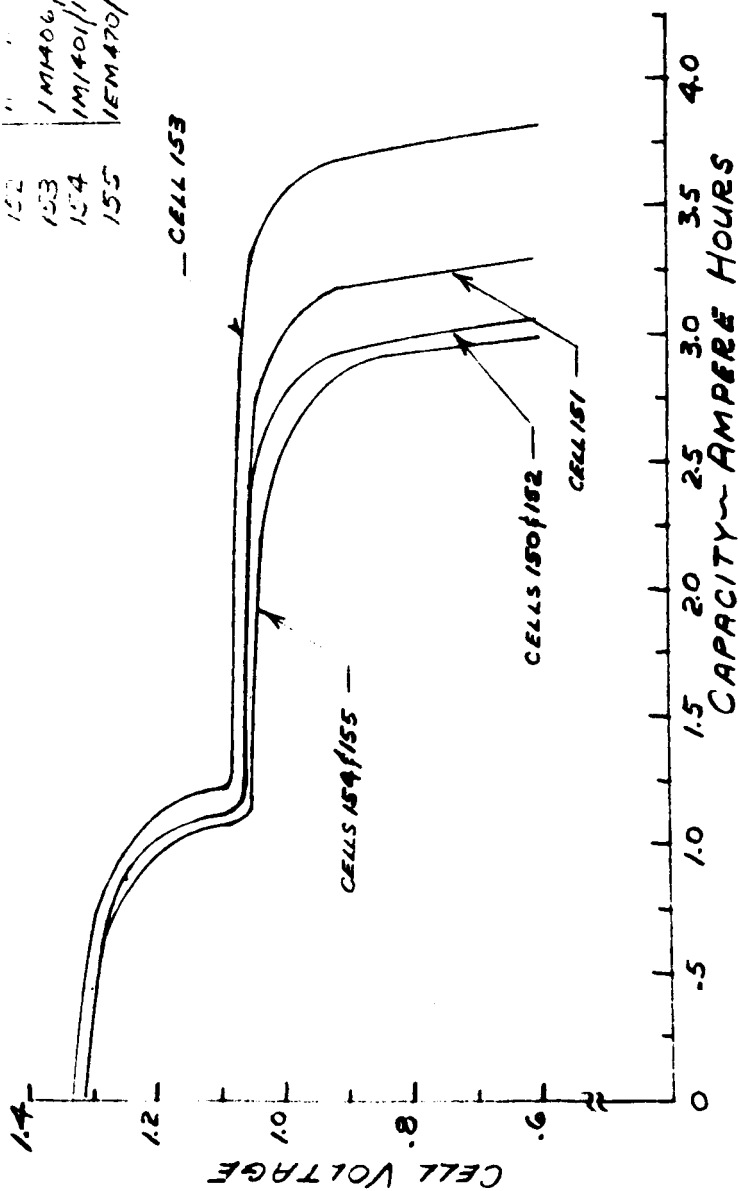
Sig.6



# EFFECT OF SEPARATOR SYSTEM ON DEEP DISCHARGE PERFORMANCE CYCLE 2 - ROOM TEMPERATURE

DISCHARGE RATE = 1.7A

CELL #	SEPARATOR SYSTEM
150	VINYL/2 VIKING
151	" 16 PUD-0300/10
152	" " FUJIFILM 100-10
153	1M400/3 VIKING
154	1M1401/1 POLYMER NA/VIKING
155	1EM470/2XFE90-50/4P-400/1M400



Sig. 8

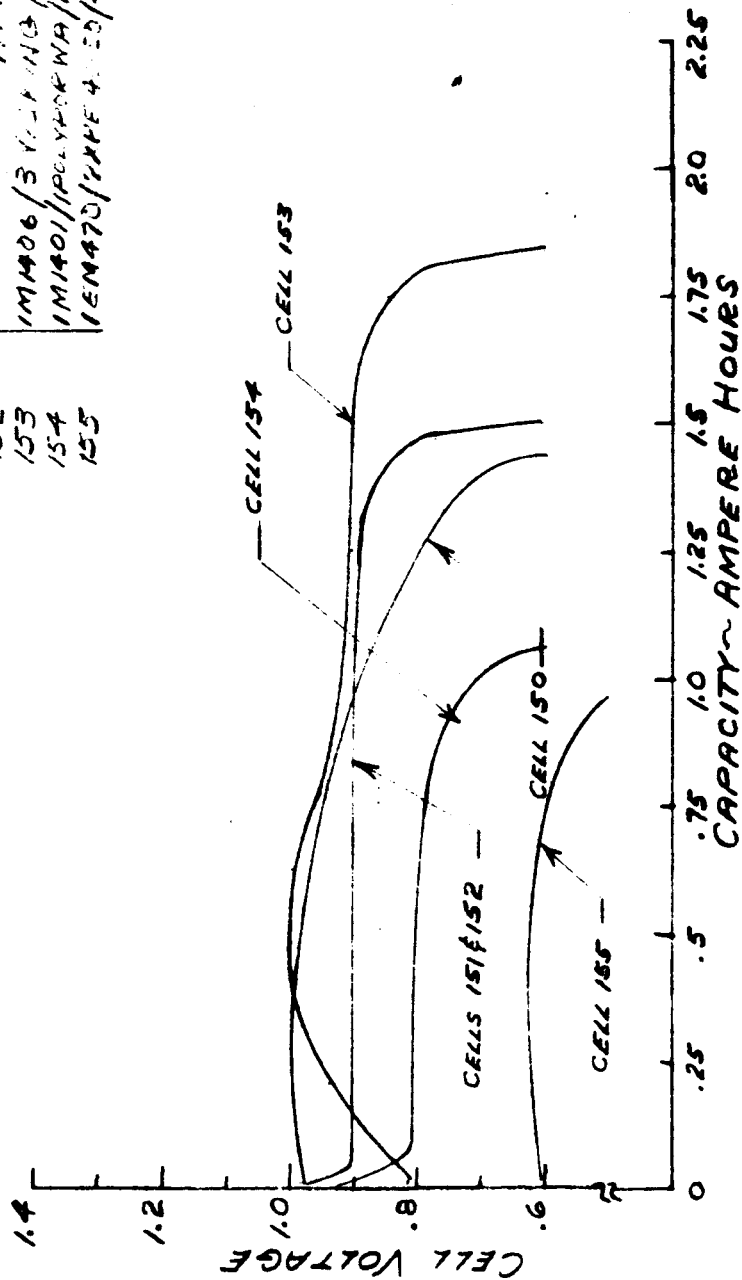


# EFFECT OF SEPARATOR SYSTEM ON DEEP DISCHARGE PERFORMANCE

CYCLE 3 -15°C

DISCHG. RATE = 1.7A

CELL #	SEPARATOR SYSTEM
150	NYR VIKING 50/11 VILKON 175L
151	" " " " " "
152	" " " " " "
153	IM406/3 VILKON 175L
154	IM1401/POLYMER WA/VILKON 175L
155	1EN470/PURFE 4.50/44-60/IM406



SEPARATOR DEGRADATION TEST-50°C  
CELLS INITIALLY FILLED WITH 42% KOH

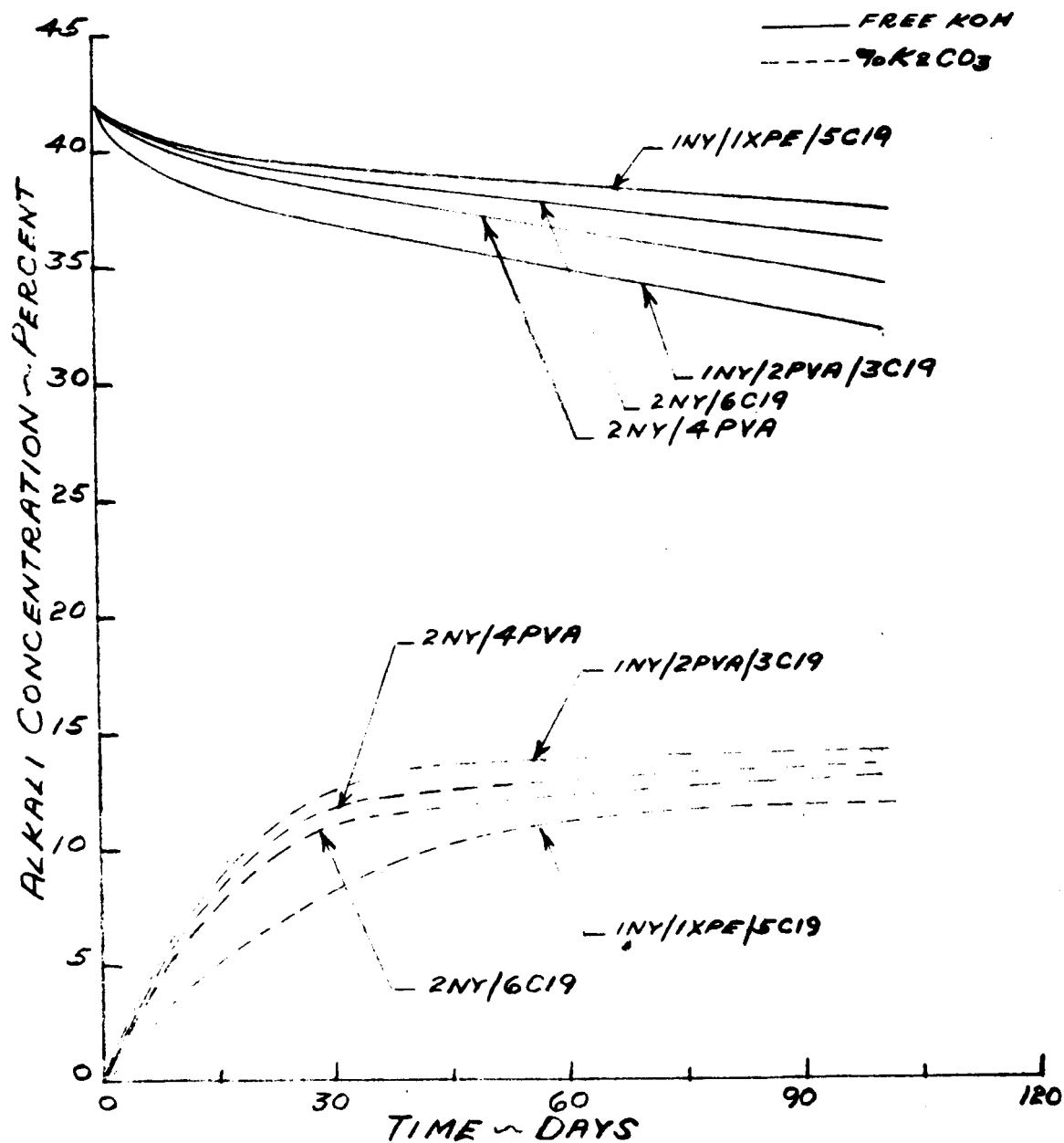
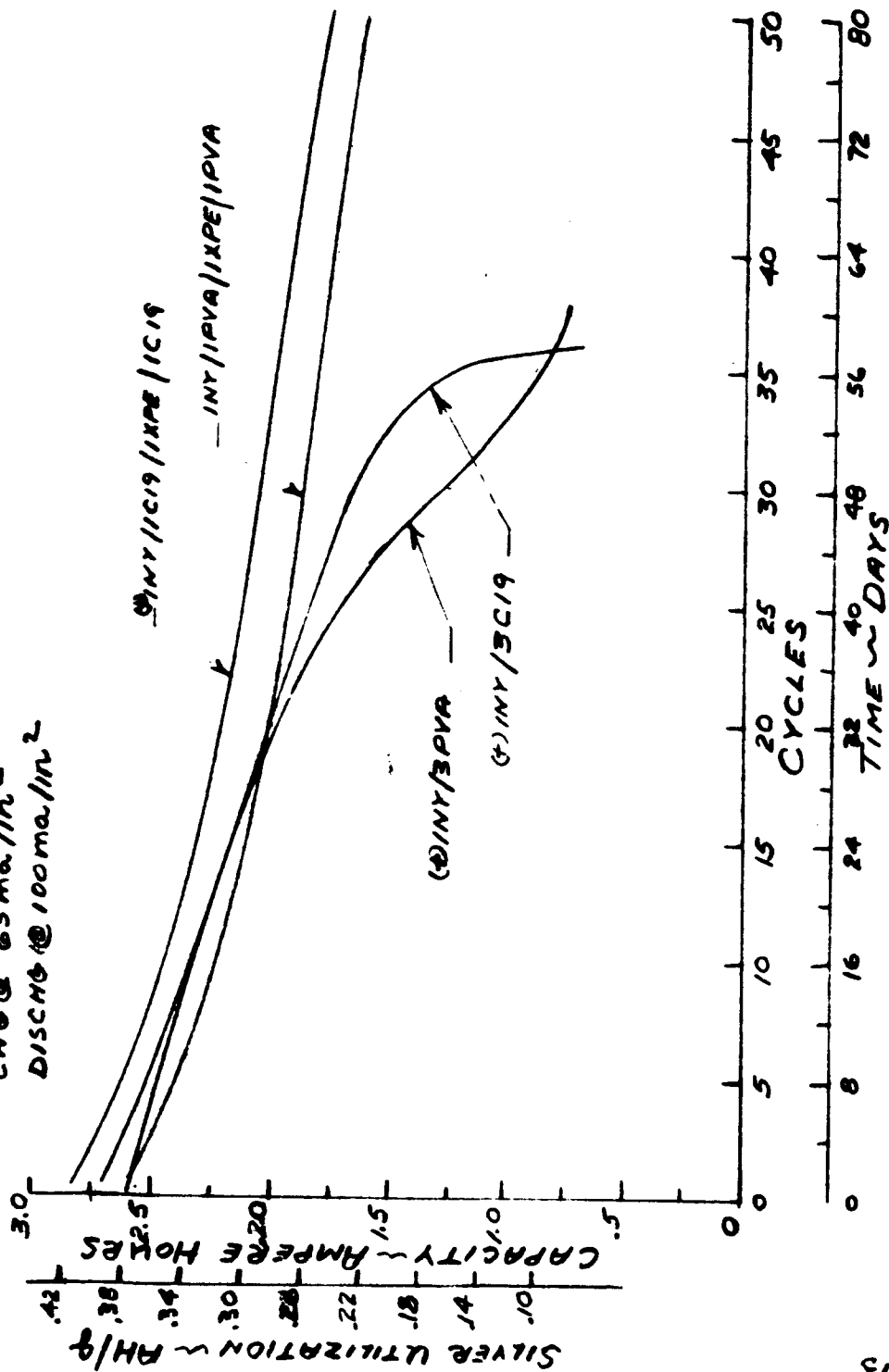


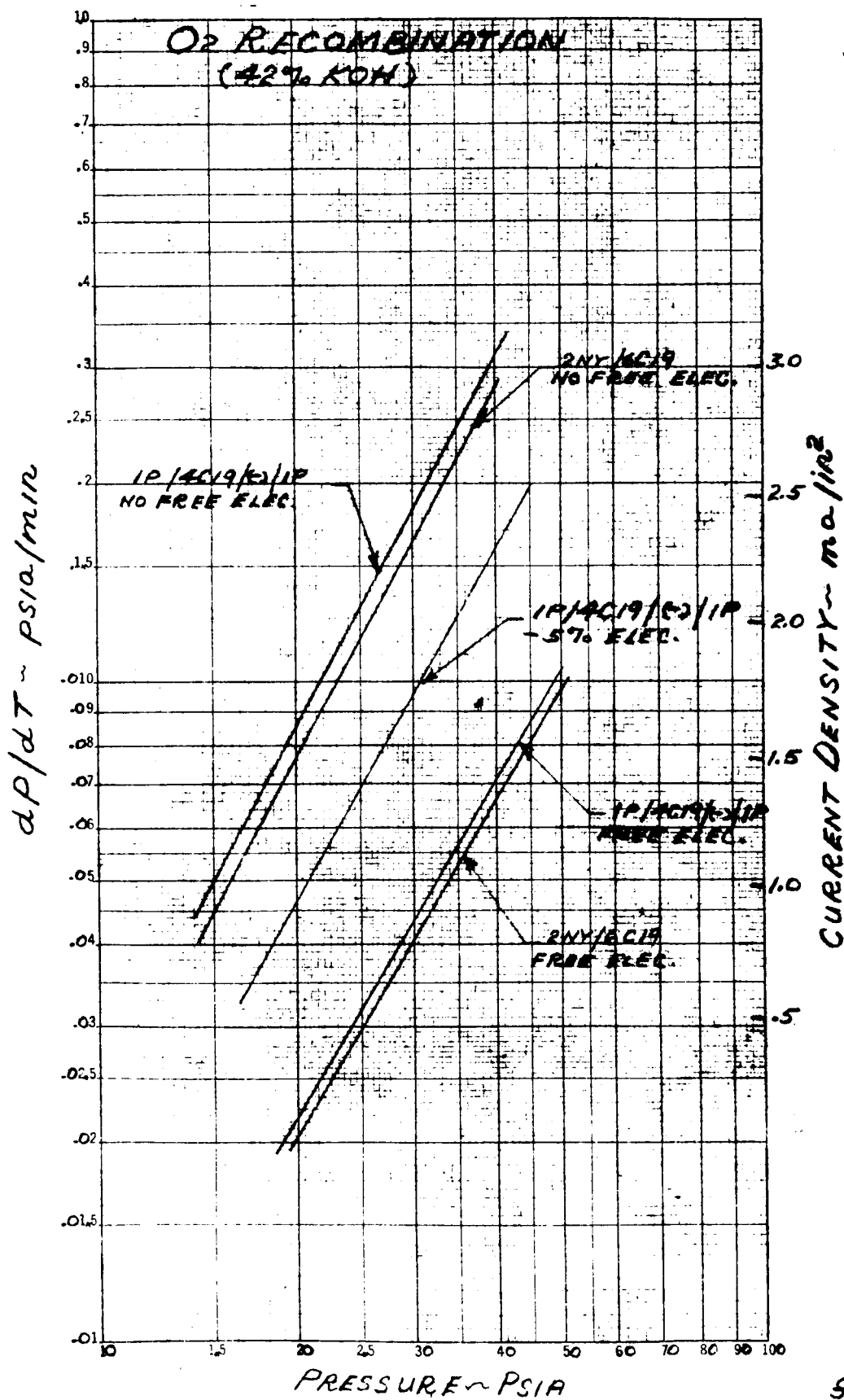
Fig. 10

# SILVER SHORTING TEST

CH @ 65ma/in<sup>2</sup>  
DISCH @ 100ma/in<sup>2</sup>



11.615



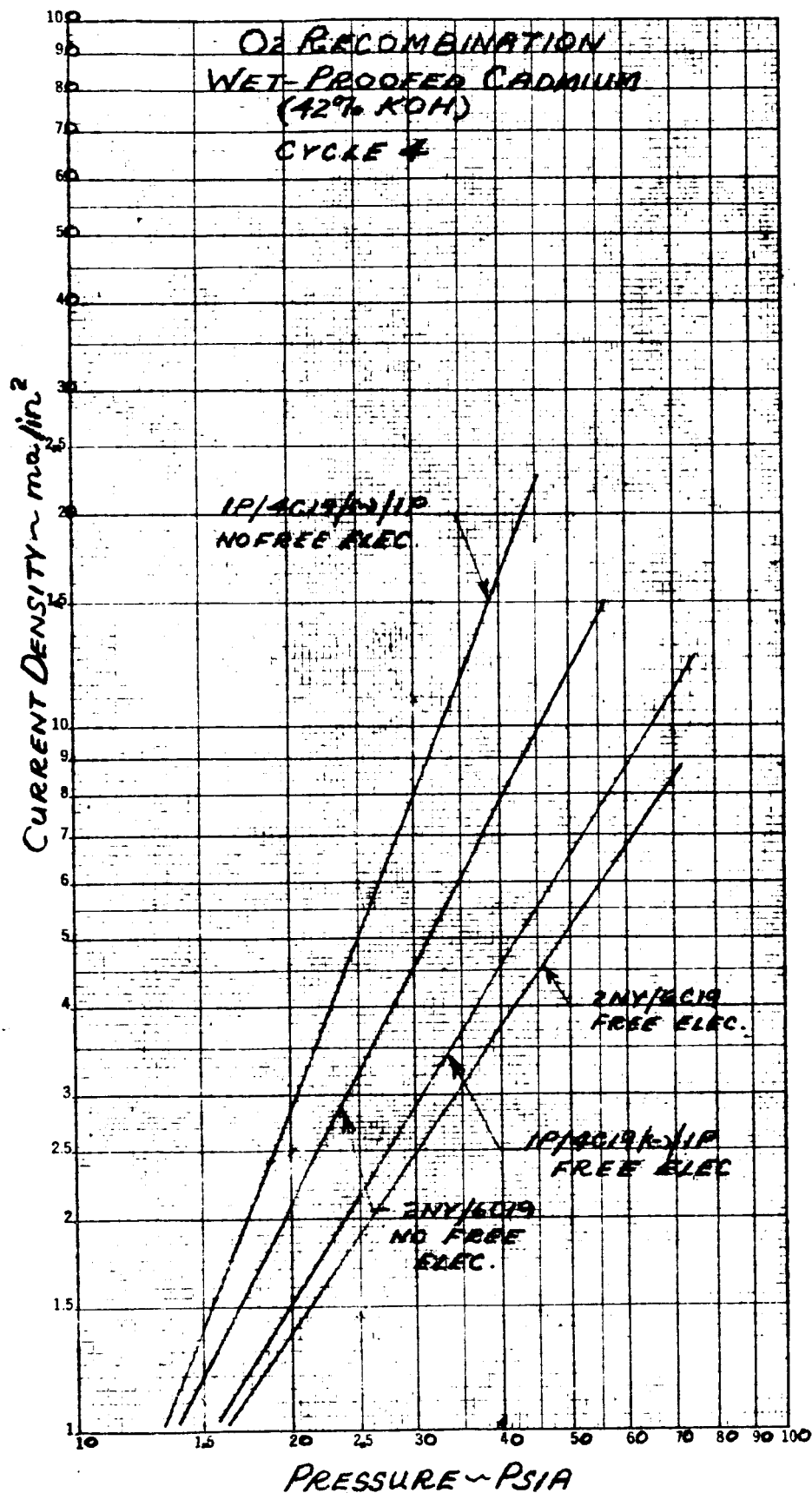
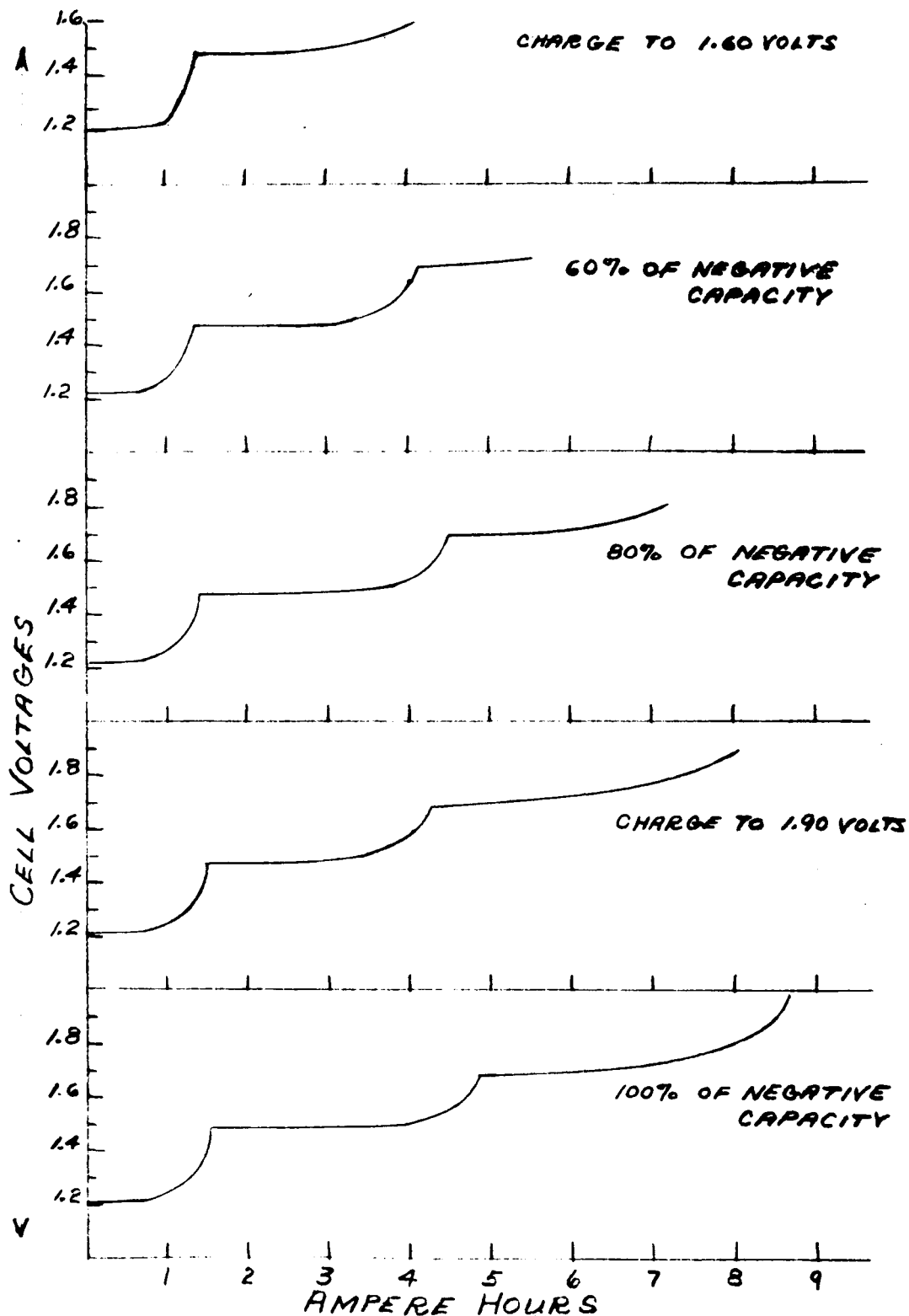


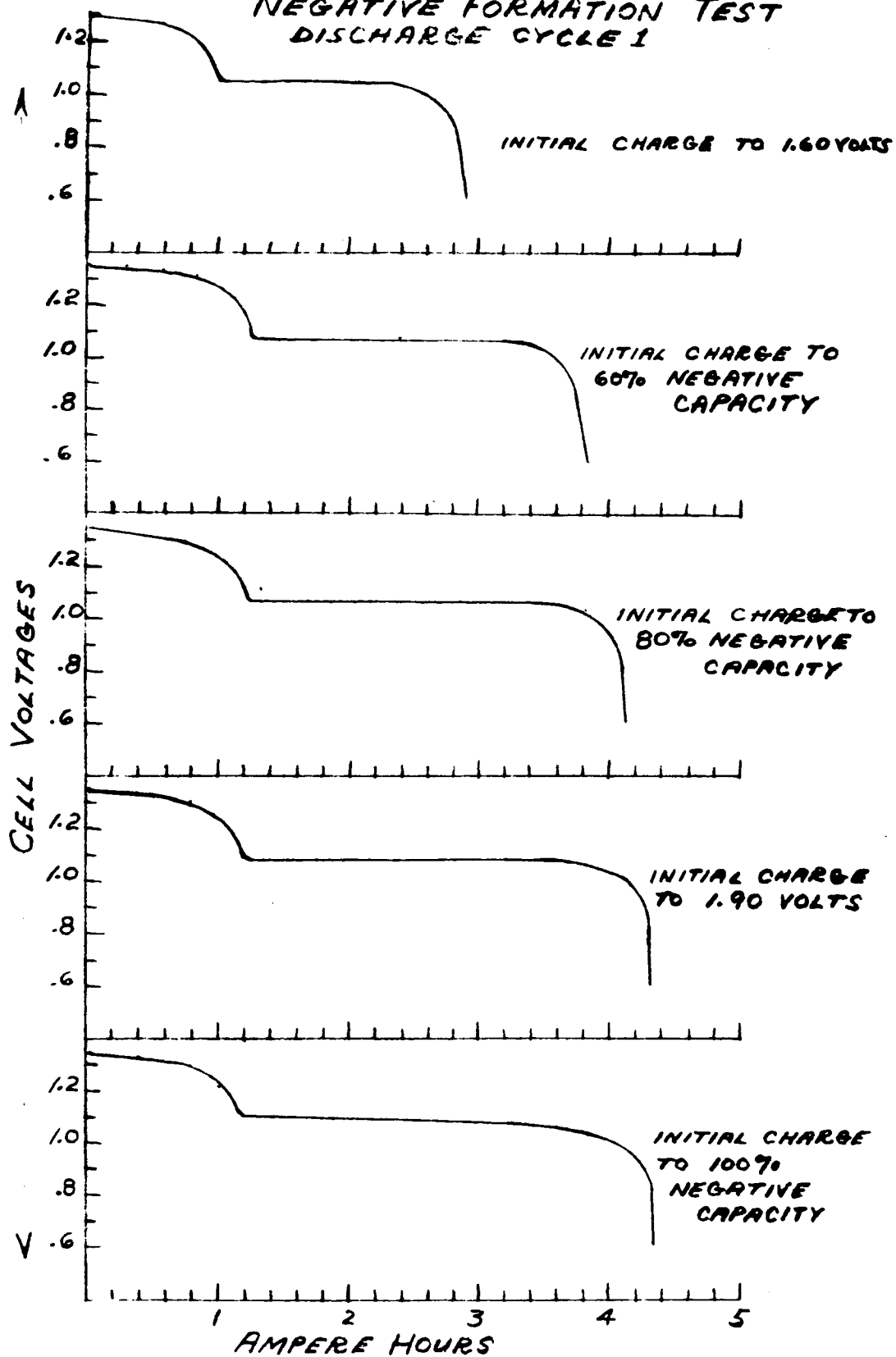
Fig. 13

# NEGATIVE FORMATION TEST CHARGE CYCLE 1



Sig.14

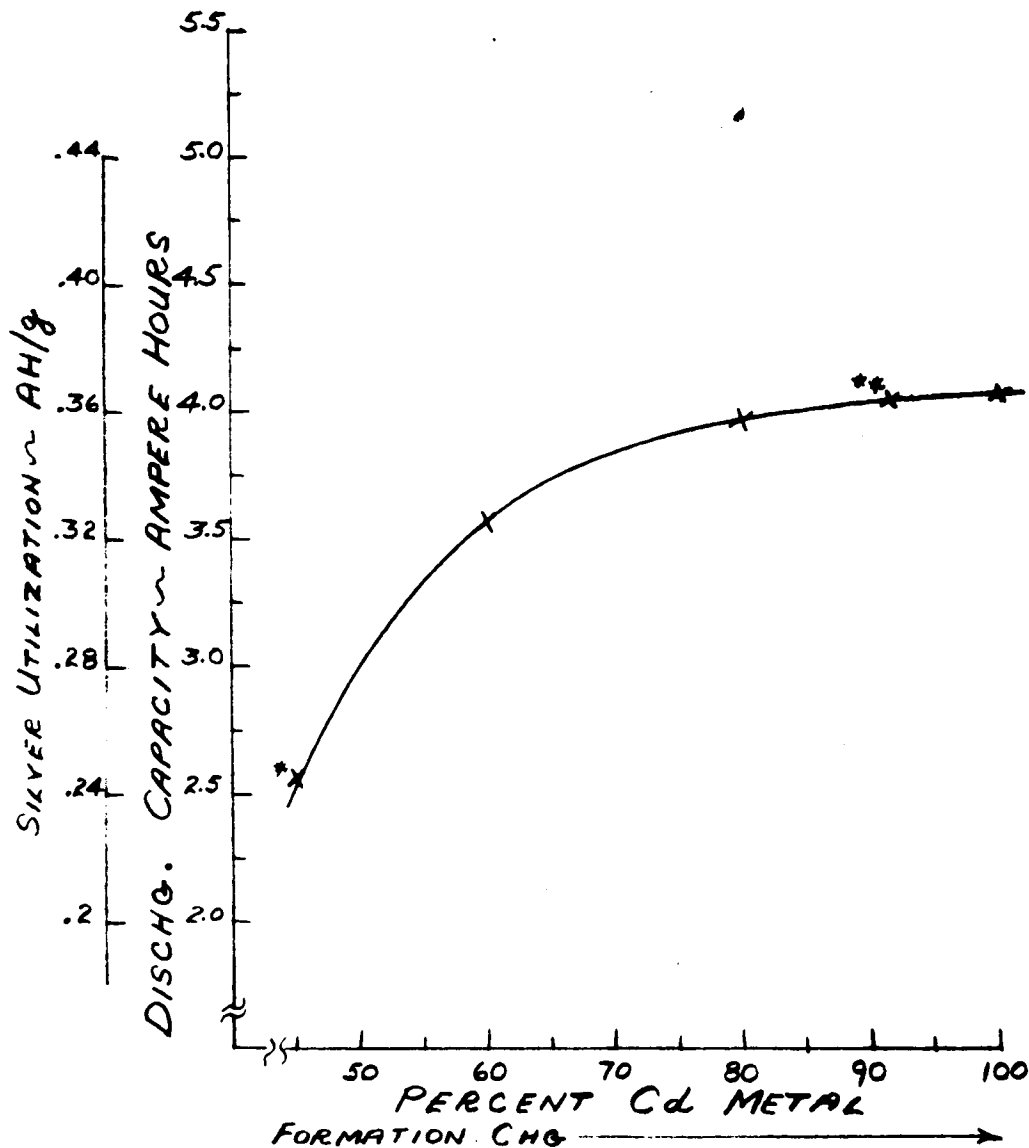
# **NEGATIVE FORMATION TEST DISCHARGE CYCLE 1**



*Fig. 15*

# EFFECT OF FORMATION CHARGE ON CELL CAPACITY

CYCLE 3  $\begin{cases} \text{CHG @ } .91A \rightarrow 1.65V \\ \text{DISCHG @ } 1.7A \rightarrow 0.6V \end{cases}$



\* 1ST CHARGE TO 1.6V  
 \*\* " " " 1.9V

NOTE: WT. OF Cd METAL EQUALS 17.7g/CELL

Fig. 16



# PROLONGED TRICKLE CHARGING CURRENT DENSITY = 0.2 MA/IN<sup>2</sup>

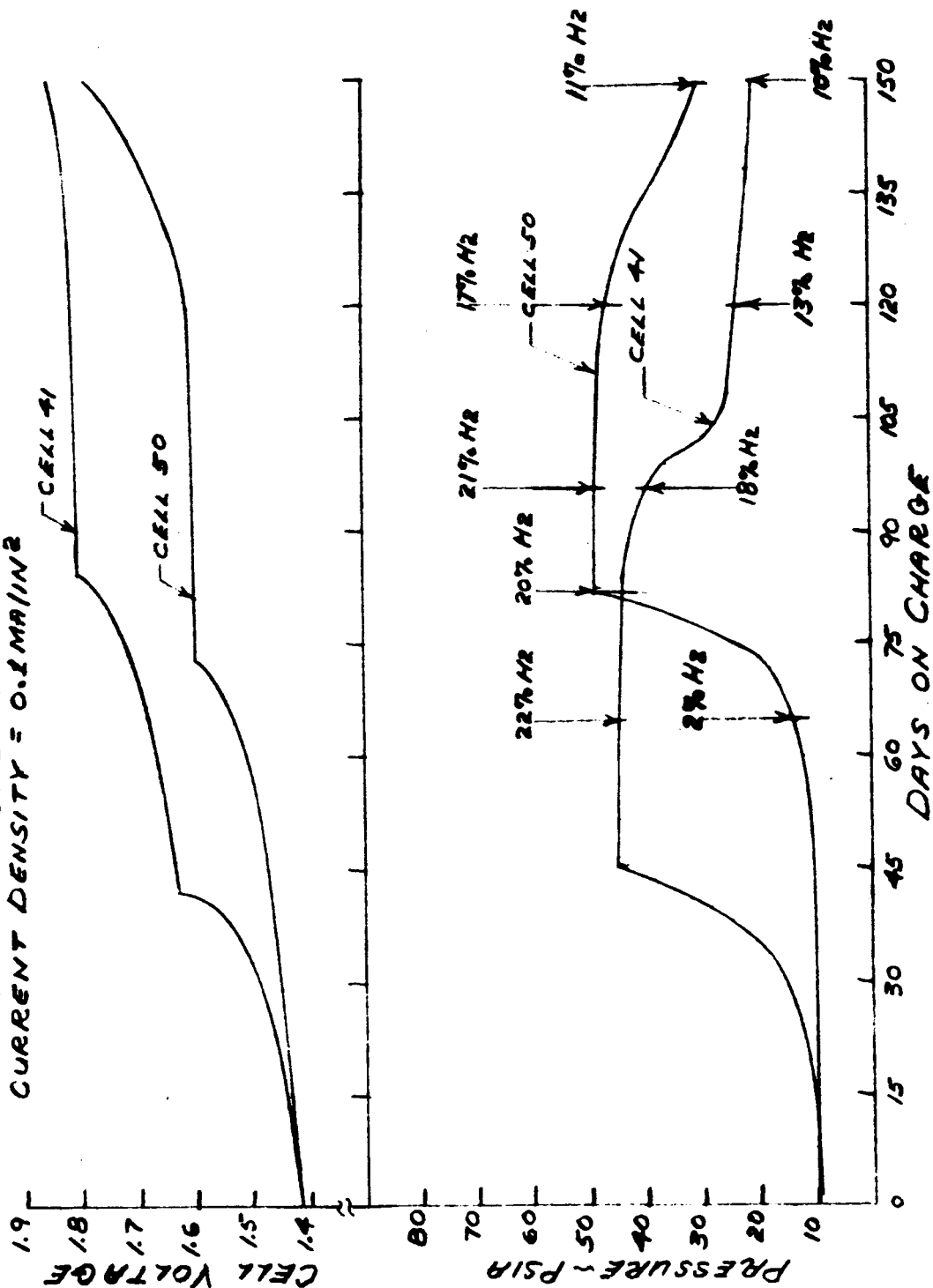
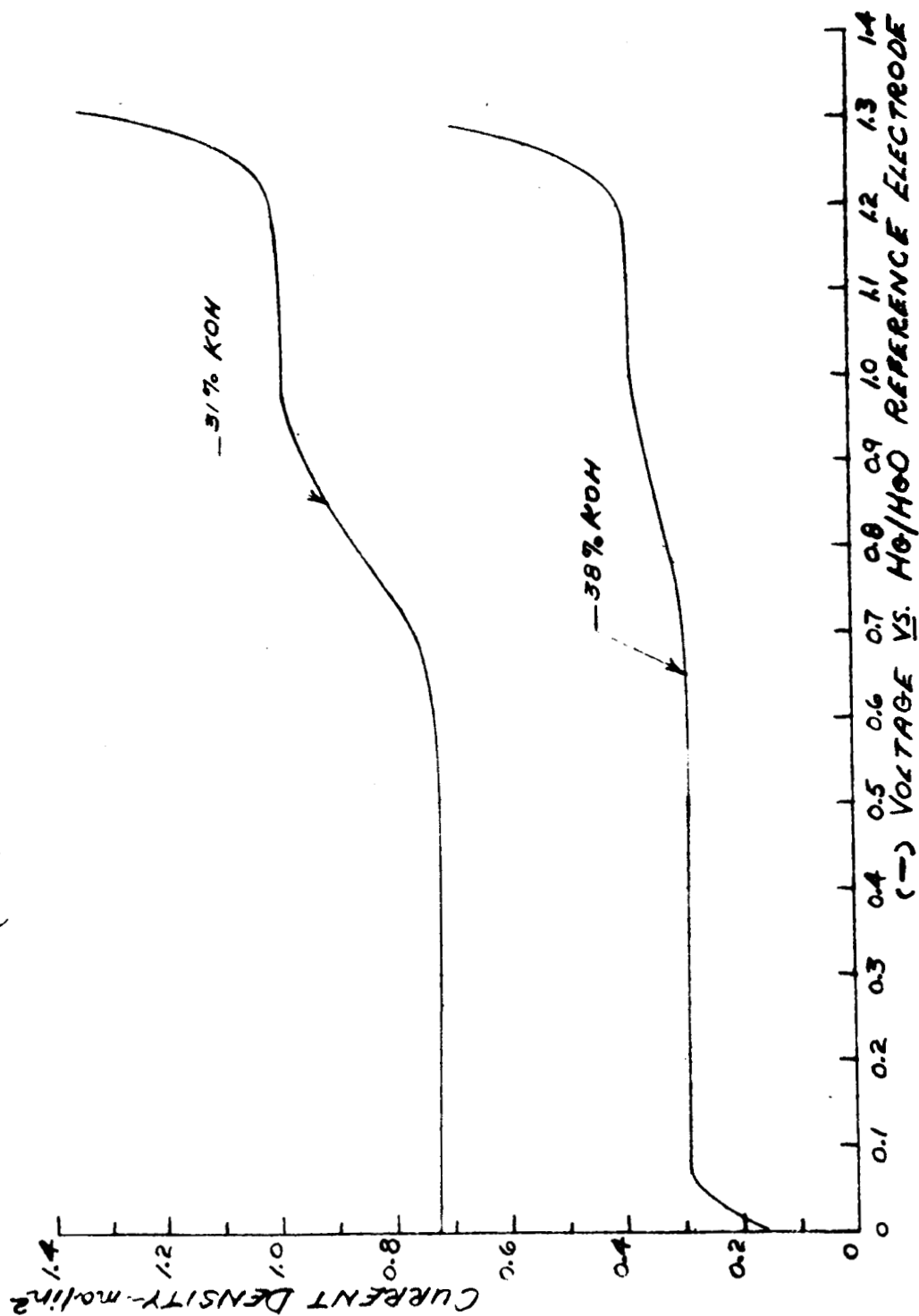


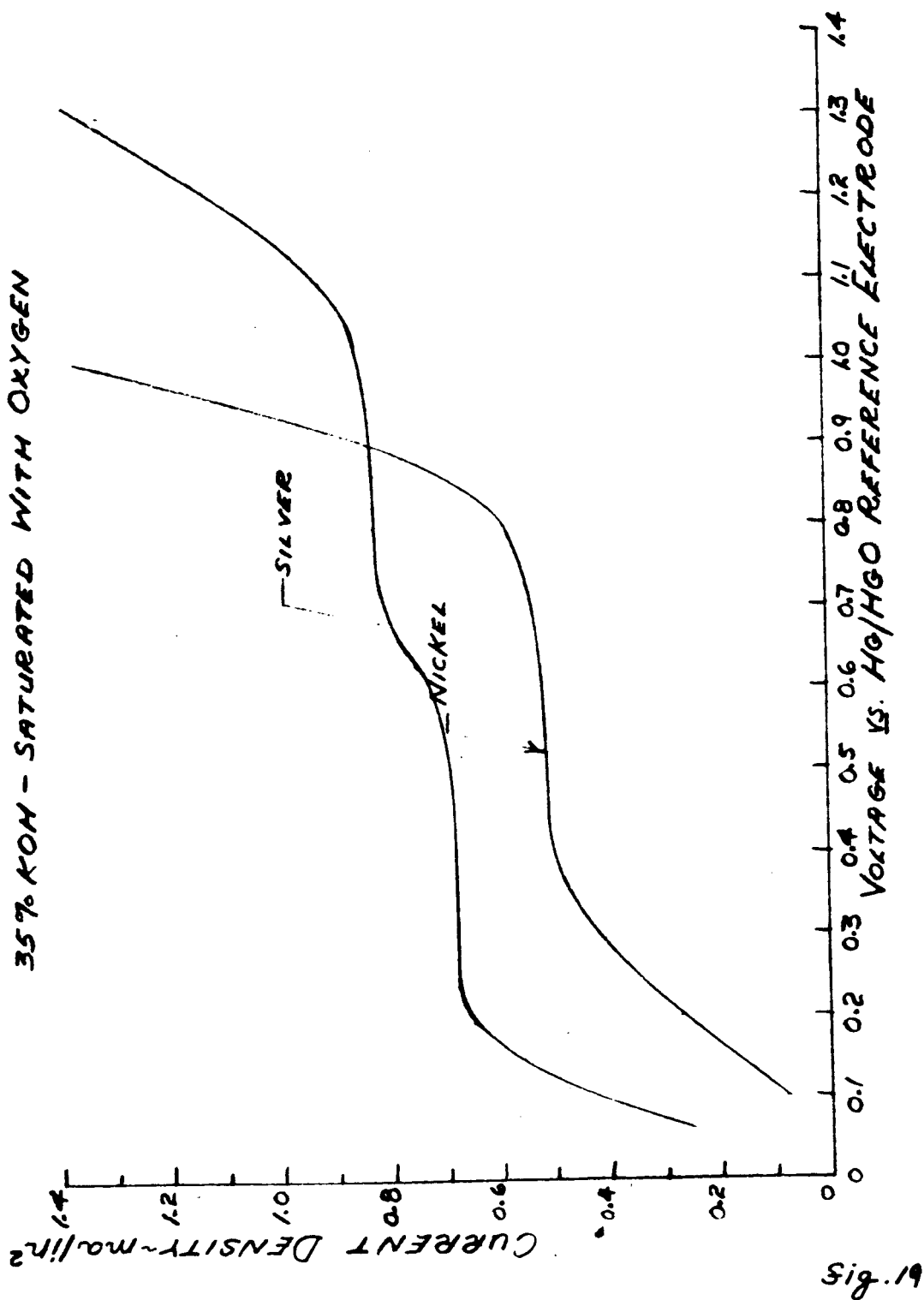
Fig. 11

# REDUCTION OF O<sub>2</sub> ON ROTATING DISC ELECTRODE (REACTION ON SILVER SHEET)



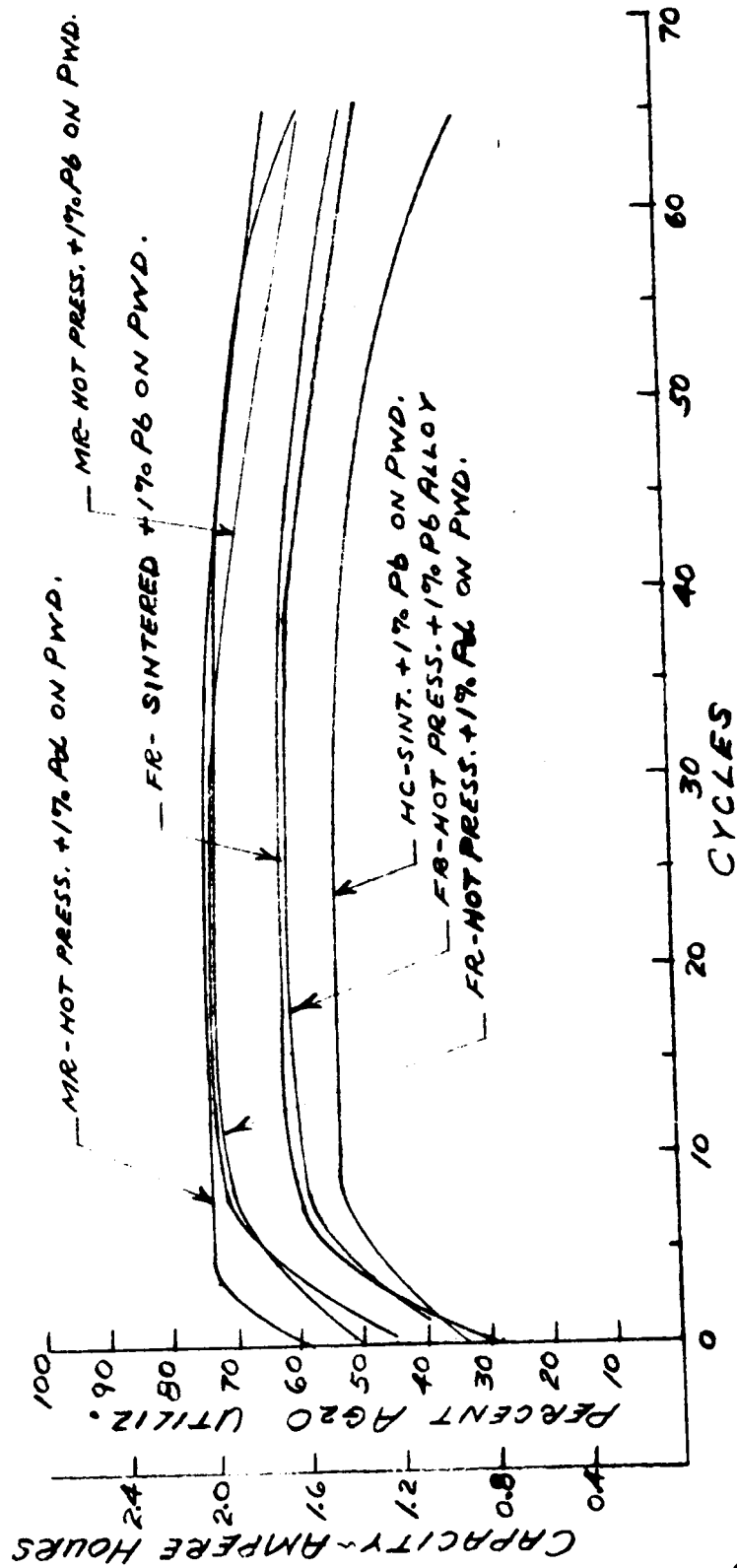
81.815

# REDUCTION OF O<sub>2</sub> ON ROTATING DISC ELECTRODE 35% KOH - SATURATED WITH OXYGEN



# SINGLE LEVEL VOLTAGE PERFORMANCE DATA

CHARGE-86 mA TO 1.35 VOLTS  
DISCHG.-2A TO 0.6 VOLTS  
CELLS FILLED WITH 42% KOH



02-815

TABLE I  
PERFORMANCE DATA - SHORT ORBIT  
(DEEP DISCHARGE AFTER 750 CYCLES)

CELL NO	AH0	AH1	LIMITING DISCHG.	ELECTRODE CHG.	CELL CONSTRUCTION
2	2.65	2.47	POSITIVE	NEGATIVE	(+) 4.8g Ag/CC, (-) 2.8g Cd/CC - 31% KOH HCl PWD (42 NY/6C19
6	2.93	2.95	"	POSITIVE	" " " " 42% KOH
8	3.13	3.08	"	"	(+) 4.2g/CC " " " " " "
10	4.10	3.92	"	"	(+) 3.6g/CC " " " " " "
*12	2.35	2.47	"	NEGATIVE	(+) 4.8g/CC HAH3 PWD " " " " " "
14	2.95	3.0	"	POSITIVE	(+) 4.8g/CC FER PWD " " " " " "
16	3.40	3.21	"	NEGATIVE	(+) 4.8g/CC (-) 2.3g/CC HCl PWD PRESS. CdO " " " " " "
18	3.73	3.68	"	POSITIVE	" " (-) 3.3g/CC PRESS. CdO " " " " " "
*22	2.98	2.86	"	NEGATIVE	" " PASTED CdO 2.8g/CC " " " " " "
*30	1.91	1.86	NEGATIVE	"	" " IMPREG. Cd " " " " " "
36	3.65	3.85	POSITIVE	POSITIVE	" " PRESS. CdO + 5% FRAG " " " " " "
38	2.96	2.98	"	"	" " (+) 2.8g/CC REVERSE PRESS. CdO WRAP " " " " " "
*68	2.86	2.73	NEGATIVE	NEGATIVE	" " " " (+) 2 PVA/3C19 " " " "
*70	3.04	3.0	"	"	" " " " 42 NY/3 PVA " " " "

\* CELLS HAVE NO FREE ELECTROLYTE

**TABLE II**  
**PERFORMANCE DATA - LONG ORBIT**  
**(DEEP DISCHARGE AFTER 70 CYCLES)**

CELL NO.	AH0	AH1	LIMITING ELECTRODE DISCHARGE	CELL CONSTRUCTION
1	2.1	2.27	NEGATIVE	(N) 4.8g/cc HCPMA W2NY/6C19 31% KOH
3	2.2	2.4	POSITIVE	" " " " " " 36.5% KOH
5	2.2	2.25	"	" " " " " " 42% "
7	2.55	2.31	"	4.2g/cc " " " " " "
9	2.92	3.0	"	3.6g/cc " " " " " "
11	2.2	2.15	"	4.8g/cc HANS PMA " " " "
13	2.16	2.21	"	" " " FR " " " "
15	2.3	2.46	"	" " PRESS. CdO 2.3g/cc " " "
17	2.71	2.91	"	" " " " 3.3g/cc " " "
21	3.33	3.45	POSITIVE	" " PASTED CdO 2.8g/cc " " "
27	3.33	3.49	"	" " " " " " " "
29	1.62	1.93	NEGATIVE	" " IMPREG. Cd " " " "
31	2.07	2.18	"	" " PRESS. CdO + 2% SHAW. BAK. " " "
33	2.05	2.27	"	" " " " GRAPHITE " " "
35	2.1	2.1	"	" " " " + 5% FB Ag " " "
37	2.07	2.05	POSITIVE	" " PRESS. CdO 2.8g/cc REVERSE WRAP
67	2.81	2.95	"	3.6g/cc (+2PVA/3C19 42% KOH
69	2.1	2.16	"	4.8g/cc " " " " " "
71	2.03	2.27	"	" " W2NY/3PVA " " "
73	2.42	2.45	NEGATIVE	" " " " 31% KOH

TABLE III  
EFFECT OF ELECTROLYTE QUANTITY ON  
CELL PERFORMANCE

CELL CONSTRUCTION	RT		-15°C		RT		+50°C	
	CHARGE AHO	DISCHARGE AHI	CHARGE AHO	DISCHARGE AHI	CHARGE AHO	DISCHARGE AHI	CHARGE AHO	DISCHARGE AHI
(W) 2NY/6C19 (C) FREE ELECTROLYTE	3.90	3.8	2.20	1.95	3.50	3.30	3.95	4.0
(W) 2NY/6C19 (C) NO FREE ELEC.	3.0	2.95	1.65	1.35	2.75	2.70	3.15	3.20
(W) PELLON/4C19 (C)/1PELLOX FREE ELEC.	3.5	3.52	1.95	1.85	3.40	3.25	3.45	3.61
(W) 1PELLOX/4C19 (C)/1PELLOX 5% ELEC. REMOVED	3.5	3.35	1.98	2.03	3.21	3.25	3.41	3.52
(W) 1PELLOX/4C19 (C)/1PELLOX NO FREE ELEC.	3.83	3.61	2.26	2.33	3.45	3.30	3.65	3.75

CHARGE RATE = 0.91A  
DISCHG. RATE = 1.7A

TABLE IV  
PERFORMANCE DATA ~ WET PROOFED CADMIUM

CELL CONSTRUCTION	RT CYCLE 1		-15°C CYCLE 2		+50°C CYCLE 4		RT CYCLE 400	
	AH0	AH1	AH0	AH1	AH0	AH1	AH0	AH1
2NY/6C19 FREE ELECTROLYTE	3.57	3.55	1.75	1.55	3.79	3.52	3.45	3.48
2NY/6C19 NO FREE ELEC.	2.85	2.72	1.45	1.32	3.05	2.95	2.62	2.51
1PELLOX/4C19(-)/1PELLOX FREE ELEC.	3.33	3.20	1.85	1.74	3.82	3.87	NO DATA AVAILABLE YET	
1PELLOX/4C19(-)/1PELLOX NO FREE ELEC.	3.42	3.40	1.80	1.82	3.85	3.94	NO DATA AVAILABLE YET	

CHARGE RATE = .91A  
DISCHG. RATE = 1.7A



TABLE V  
OXYGEN RECOMBINATION

DISC MATERIAL	CONST. POTENTIAL VS. Hg/HgO	KOH CONC. %	* CURRENT DENSITY μA/cm <sup>2</sup>	RATE CONST. cm/sec	LIMITING PROCESS
Cd	OPEN CIRCUIT	31	4.2	$0.7 \times 10^{-4}$	KINETIC
Cd	-0.85V	31	4.2	$0.7 \times 10^{-4}$	KINETIC
Cd	-0.90V	38	3.6	$1.0 \times 10^{-4}$	KINETIC
Cd	-0.95V	38	8.8	$2.4 \times 10^{-4}$	KINETIC
① Ag	-0.95V	38	32.0	$8.6 \times 10^{-4}$	DIFFUSION
② Ag	-0.95V	38	~5	$\sim 10^{-4}$	KINETIC

\* CALCULATED FROM RATE OF O<sub>2</sub> CONSUMPTION

① - 0 - 2 MINUTES

② - AFTER 2 MINUTES